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Aniline-furfural stabilization of Iowa loess

John Briggs Sheeler
Iowa State College

ANILINE-FURFURAL STABILIZATION OF IOWA LOESS

by

John Briggs Sheeler

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Signature was redacted for privacy.
Heads of Major Departments

Signature was redacted for privacy.
Dean of Graduate College

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INTRODUCTION

The term soil stabilization refers to any process by which soil is made stronger and more resistant to deformation and displacement under applied load and more resistant to the natural forces of weathering.

Soil stabilization has been an art and in its broadest sense can probably be traced as far back as the origin of man. The science of soil stabilization as a systematic effort based on fundamental knowledge has been developed almost entirely within the past quarter century.

Gravel and crushed rock have been successfully used in the construction of bases and sub-bases for highways and airports but many areas are either devoid of these materials or have had their supply exhausted. Use of materials from distant areas is precluded by the cost of transportation. One solution to this problem is the utilization of local materials such as soil. Most soils are not naturally suited for base courses and therefore require stabilization. Southwestern Iowa is an area in which the above situation exists.

Since 1950 the Iowa Engineering Experiment Station at Iowa State College has been conducting studies of fundamental properties and stabilization methods on Iowa soils. These

studies have been directed toward efficient and economic methods of suitable base and surface course construction of secondary roads. The work is being carried on under contract with the Iowa Highway Research Board and is supported by funds from the Iowa Highway Commission and the U. S. Bureau of Public Roads.

Early stabilization studies indicated that artificial resins were possibilities in accomplishing a practical stabilization with satisfactory results. The most effective of these artificial resins was a resin formed by the reaction of two parts aniline to one part furfural.

Aniline-furfural resin was tried on Southwestern Iowa loess as an exploratory measure with results that indicated further study was warranted. The purpose of the investigations described herein has been to determine and evaluate the optimum conditions and additives necessary to satisfactorily stabilize Iowa loess with an aniline-furfural resin.

REVIEW OF LITERATURE

The stabilization of soil with aniline-furfural is accomplished in much the same manner as is used in impregnation. The resin is produced after the non-resinous materials have been mixed in with the soil. The concept of resin formation is essential in understanding this type of soil stabilization and is therefore presented in this review.

General Consideration of Resins

The term "resin" and the term "plastic" are sometimes used as synonyms which leads to confusion. Resins are the raw materials from which plastics are made. The synthetic resins are frequently polymers of a recurring structural unit. They do not form a specific compound because the number of recurring units in each chain is not constant. Resins are the essential base material in all plastics and in most coating materials and adhesives.

General usage of the word "plastics" has dictated that the meaning applies to materials that have a relatively high molecular weight, are organic in nature, and have been or can be formed by heat and pressure or by pressure alone and will retain their shape under normal conditions of

temperature and pressure. A plastic object frequently has been in the liquid state or in solution before and during the forming operation. In order to make a finished plastic article it may be necessary to mix pigments, fillers, plasticizers, and other modifiers with the resin before it is molded.

The formation of higher molecular weight substances from smaller units is classified into two distinct and carefully defined reactions. These reactions are condensation and polymerization, however both are generally termed as polymerization reactions.

Polymerizations are defined as those reactions which yield a product that is an exact multiple of the original molecule. This type of polymerization is called addition polymerization. A second type in which two different molecules add is called copolymerization. The polymerization of vinyl acetate and vinyl chloride is an example of the latter type.

Condensations take place by the uniting of two or more molecules with the subsequent loss of a small molecule. A simple example is found in the reaction of acetic acid and ethyl alcohol to produce ethyl acetate and water.

One of the many uses of resins is in the role of an impregnating agent. Impregnation may best be distinguished from coating and the application of adhesives by the fact

that the entire body of the material is altered in character rather than just the surface. Many coatings and adhesives penetrate into the material to which they are applied but their primary purpose is to alter or bind the surface only.

One of the best examples of an impregnating agent that completely alters the character of the material is in the impregnation of a soft wood with methylol urea, the monomeric unit of urea-formaldehyde resins, and then carrying out the polymerization reaction in the cells of the wood. The product will not swell, shrink, or warp with humidity changes, and the grain will not rise on wetting. The material can also be worked, turned, and finished to give a product superior to the hardwoods.

There are many applications in this field that are not in use at the present time and the field is rapidly expanding. In many cases the use of impregnating agents is curtailed due to the belief that the added expense is not warranted or that the improvement in quality is not justified. Improvement in quality is certainly the main contribution of impregnating agents in every case.

Previous Work

The use of aniline-furfural resins as a soil stabilizer has been investigated by Winterkorn (42) as a part of a

study done under contract with the Civil Aeronautics Administration. He later extended the use of the resin to the stabilization of beach sand (43). On the basis of the first laboratory study Winterkorn concluded that two combinations of aniline-furfural gave reasonably good resin binders. These combinations were in ratios of 70:30 and 35:65 parts by weight of aniline and furfural. The 70:30 resin was found to be stronger and to withstand weathering better.

The addition of iron and aluminum salts was found to slightly improve resin strength. Both resins were found to produce poor results when used in alkaline mixes. Acid mixes resulted in maximum strengths. Foaming agents were found to be unsuccessful in improving the strength of specimens.

Winterkorn has further concluded that the 70:30 resin was most effective in medium plastic soils with the small amounts of the used. The resin acts as both a binding and a waterproofing agent. The ability of the resin to perform these two functions is considered to be quite significant in admixture quantities of as little as 2 per cent.

Geiseking (18, p. 75) presents a discussion of the alteration of clay properties by organic cation adsorption in which he states that naturally occurring cations may be replaced by large organic cations and that the nature of the

organic cations influences the water affinity of the soils. The most common organic cationic compounds are the amines. Geiseking has also shown that clays saturated with various organic cations do not adsorb as much moisture as the corresponding natural clays. Results reported by numerous other authors also show that organic-ammonium-saturated clays are more hydrophobic than natural clays.

E. H. Goebel (18, p. 78) discusses the aspects of aniline-furfural soil stabilization in terms of organic cations. He states that a 2 aniline to 1 furfural compound is a large organic cation and acts in accordance with Gieseking's explanation of the effect of such cations on the water affinity of soils. Goebel also points out that a polar compound of this type has a tendency to polymerize due to its large number of double bonds. The double bonds indicate a site of great chemical activity because of their unsaturated character. The reaction of aniline and furfural is discussed later in this dissertation.

A report by Mainfort (25), on the use of a number of chemical admixtures for soil stabilization, includes data and comments on the use of aniline-furfural. Maximum stability was attained when the chemicals were added separately to the soil after the required mix water had been incorporated or when the two chemicals were added to the dry soil in separate portions of the water.

The reaction between aniline and furfural was slow in moist soil. They found that treated soil could be easily molded within at least 8 hours after mixing. Samples that were moist-cured prior to testing were always inferior to air-cured samples.

The aniline-furfural treated soil specimens were superior to all other chemical admixtures tested with the exception of portland cement. In tests where aniline-furfural treated specimens were oven-dried before exposure they proved superior to samples treated with even higher percentages of cement.

A laboratory comparison of aniline-furfural and several other stabilizing admixtures was made at Iowa State College in the fall of 1955 under the supervision of Mr. R. K. Katti. The laboratory study was performed as an integral part of a graduate course in soil stabilization, which was taught by Professor D. T. Davidson of the Civil Engineering Department. All specimens were 2 in. in diameter by 2 in. high and were molded at modified Proctor density using 25 blows from a 5 pound hammer dropped from one foot above the specimen. Lime and fly ash, lime, portland cement, Arquad 2 HT, bituminous materials, and aniline-furfural were compared.

The strength of specimens treated with 5 per cent aniline-furfural remained constant at near 2000 pounds through 12 cycles of freezing and thawing. The portland

cement stabilized specimens showed a strength gain from 2300 pounds to 3200 pounds while all other specimens were very weak or failed entirely. Moisture absorption was the lowest in the aniline-furfural treated specimens.

A study of the effect of wetting and drying produced similar results with aniline-furfural again showing good waterproofing qualities. The Arquad 2 HT also exhibited good waterproofing.

A curing time study revealed a steady increase in strength as determined at 7, 14, 21, and 28 days for the aniline-furfural treatment. A decrease in moisture absorption with time was also noted. The increase in strength with time occurred with all admixtures that depend on a chemical reaction for stabilization.

INVESTIGATION

The initial investigation of aniline-furfural stabilization was based on results of prior research done by other investigators. Neither the moisture-density relations nor the effects of moisture on strength were available for loess soils. Mainfort (25) reported the moisture-density relationships for two aniline-furfural stabilized soils in which optimum moisture with the resin admixture was near the optimum moisture for soil alone. Winterkorn (43) found that a ratio of about 2 mols aniline to 1 mol of furfural produced near optimum resin quality. In view of these findings it was decided that the first investigations should employ a 2:1 mol ratio of aniline to furfural in the determination of moisture-density relationships.

Properties of Soils and Chemicals

Geological aspects of loess in southwestern Iowa are considered to be pertinent to the existing problem and are therefore included in this section.

Wisconsin loess in southwestern Iowa

The soils employed in this investigation came from the southwestern portion of Iowa where composite Wisconsin loess forms a massive surface deposit that mantles older loesses and pre-Wisconsin glacial deposits. Available evidence indicates that the main body of the loess is a wind-blown material. Major sources of supply were probably the flood plains of valleys draining the glacial drift areas and the exposed surfaces of newly deposited drifts. Four glacial drifts of the Wisconsin stage, Iowan, Tazewell, Cary, and Mankato, are believed to have contributed to the formation of the composite Wisconsin loess (also called Peorian loess in geological literature).

The sampling area included in this investigation is shown in Figure 1. The thickness of the Wisconsin loess, as measured on ridges and hilltops, varies from 60 to over 100 feet along the Missouri River bluffs to about 17 feet at the arbitrary eastern boundary as shown in Figure 1. The depth measurements include the thickness of the A and B horizons where both are present. The principal soil association areas in this portion of the Wisconsin loess are the Monona-Ida-Hamburg and the Marshall (33). The solum on the hilltops and ridges varies from zero or a few inches in depth along the west boundary to three or four feet near the east

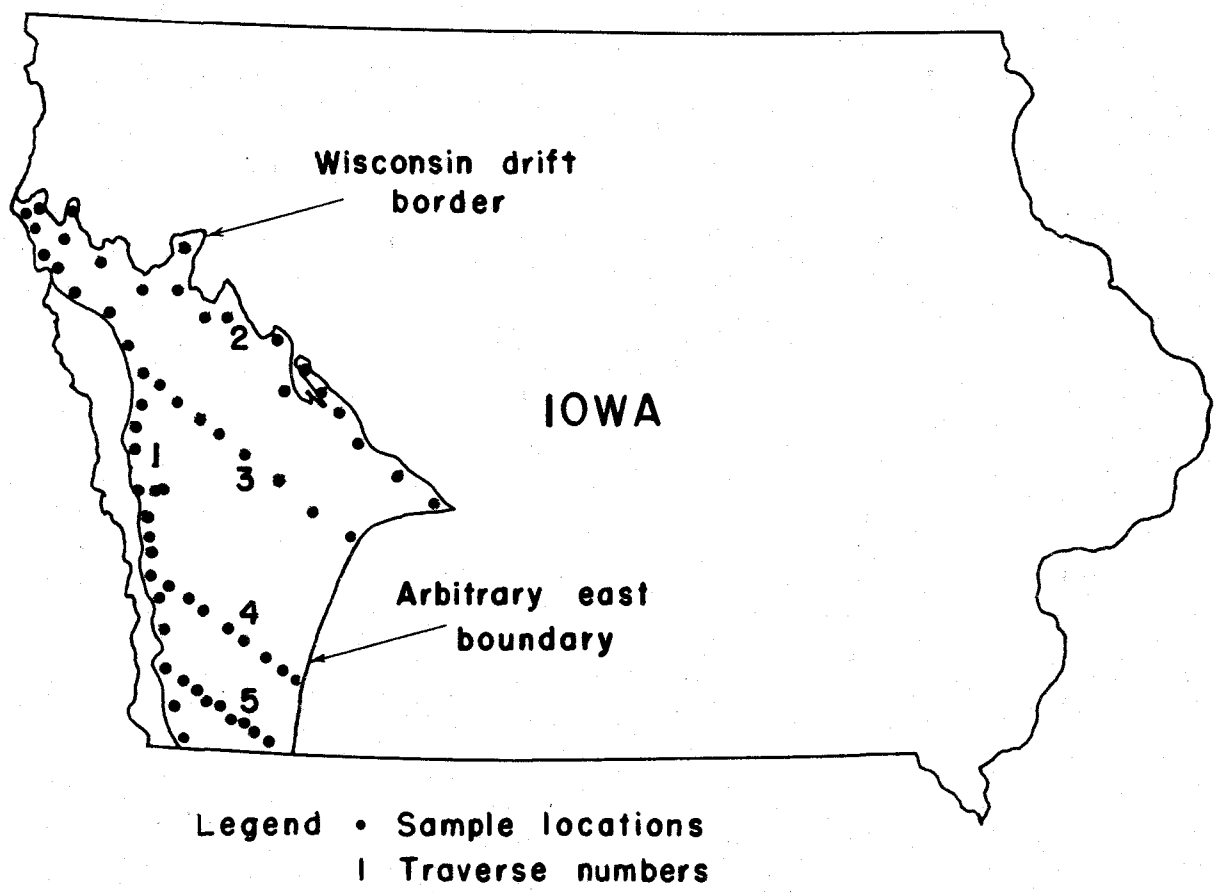


Figure 1. Locations of sampling traverses in Wisconsin loess of southwestern Iowa

boundary.

Over one hundred samples of Wisconsin loess have been taken along the five traverses shown in Figure 1. Comtrol samples for determining areal property variations were taken at a depth of from two to three feet below the top of the C horizon at each of the locations shown on the map. Traverses 3, 4, and 5 were laid out to parallel, what is believed to represent with a reasonable degree of accuracy, the direction of the generally prevailing winds during the loess deposition time. Traverse 1 follows the east valley wall of the Missouri river and traverse 2 is just south of the Wisconsin drift border.

Areal and stratigraphic variations in properties were determined by comparison and correlation of results from some 25 to 30 physical and chemical tests (7). The following discussion of properties of Wisconsin loess in southwestern Iowa is based on these test results.

The loess is a fine textured soil material consisting predominately of particles of silt and clay size. The dry Munsell color of the oxidized loess is pale yellow, light yellow brown, or light olive brown. The unoxidized loess is light gray. Near its source where it is deepest, the loess is highly calcareous. As distance increases away from its source, the loess becomes thinner, finer textured, more weathered, and less calcareous. Wisconsin loess shows essentially no stratification and a characteristic feature

is its ability to stand in vertical or near vertical slopes.

The test data for traverse 1 indicate that physical and chemical properties along the east valley wall of the Missouri river are remarkably uniform both areally and stratigraphically, for a natural deposit of soil material.

With increasing distance away from the east valley wall, however, test data for samples taken along traverses 3, 4, and 5 reflect a marked increase in plasticity, shrinkage, water-holding capacity, and in-place density. The data of traverse 2 show the same general trend. These property changes appear to be chiefly due to an increase in the amount of clay in the loess (9). The textural classification of the loess changes from silty loam at the west boundary to silty clay at the east.

The mineralogical nature of the Wisconsin loess in southwestern Iowa seems to be quite uniform. Organic matter and soluble sulfate contents are low or nonexistent. Aside from variation in amount of clay, the principle variable in the loess appears to be carbonate content which varies both areally and stratigraphically. Carbonate contents, expressed as per cent calcium carbonate by weight, were as high as 18 per cent along the east valley wall of the Missouri river and decreased to as low as one per cent in samples near the arbitrary east boundary.

The loess may be conveniently divided into two fractions of minus 5 micron material and plus 5 micron material. In general the plus 5 micron material contains mostly quartz, feldspar, and calcite along with a minor amount of heavy minerals. These minerals are considered to be non-reactive with large organic cations.

The minus 5 micron material in the loess is very similar throughout and consists mainly of clay minerals. The clay minerals in this fraction are thought to exist as a randomly interstratified mixture of montmorillonite and illite types. X-ray diffraction data indicate an increase in the montmorillonite:illite ratio with increasing clay content in the loess.

Microscopic examination of the loess has shown that the clay occurs mainly as coatings on larger grains. This tends to increase the effectiveness of the clay.

Cation exchange capacity is one of the most important properties of soil, a fact that has long been recognized by agricultural soil scientists (20). It can be measured quantitatively and is closely related to the physical and chemical behavior of soil. It has been related to engineering properties of Wisconsin loess (8). On the basis of over one hundred samples of Wisconsin loess, the range in cation exchange capacity values in the southwestern Iowa area is 7.5 to 25.8 milli-equivalents per 100 grams of soil.

The exchange capacity of the loess is the lowest near the major source of the loess and increases in value with distance eastward away from the source. This increase is mainly attributed to an increase in the amount of clay in the loess.

Soil samples

In view of the orderly variation of areal and stratigraphic properties of southwestern Iowa loess and the apparent qualitative mineralogic continuity, it was decided to investigate the effectiveness of aniline-furfural stabilization on this soil by studying a few samples representing the entire area. The soil samples were selected to provide a range in clay content from a silty loam to a clay and to represent the carbonate range of 7.6 per cent to less than 1 per cent.

Initially samples 20-2 and 44A-1 were used in obtaining some basic data necessary for further study. Several hundred pounds of each soil were obtained from the C horizon with the exception of sample 503-2 which was from the B horizon. The locations of the samples are indicated in Table 1. Sample 20-2-II is from a different stratigraphic position than 20-2 and was used since it affords a better position in the overall representation of the range in soil properties of the loess.

Table 1. Location of loess samples

Sample no.	County	Township	Section	Soil series	Thickness of solum,[1] ft.	Sampling depth below surface, ft.
55-1	Harrison	Little Sioux	8	Hamburg	½	2½-3
20-2	Harrison	St. Johns	15	Hamburg	0	60-61
20-2II	Harrison	St. Johns	15	Hamburg	0	34½-35½
26-1	Shelby	Grove	21	Monona	2	4-5
36-1	Montgomery	Grant	14	Marshall	3½	5½-6½
44A-1						
46-1	Page	Amity	30	Marshall	3	5-6
503-2	Taylor	Jefferson	17	Sharpsburg	4	1½-2

[1] Solum includes the A and B horizons where both are present

The soil samples were selected from laboratory data obtained from small exploratory samples used in the initial phases of Project 283-S. The samples were selected to present a range in clay content that rose in increments of approximately 5 per cent. This was borne out by subsequent analysis of representative samples taken from the larger samples used in this study. The lone exception was sample 46-1 which shows a clay content very close to that of 36-1.

Table 2 lists the important physical and chemical properties of the samples. A thorough discussion of the geology, pedology, and important characteristics of the loess soils in southwestern Iowa is presented by Davidson and associates (5, 6) in Iowa Engineering Experiment Station Reports 16 and 22.

Furfural

The discovery of furfural was made by Dobereiner in 1830 (10) while preparing formic acid by the action of sulfuric acid and manganese dioxide on sugars. Stenhouse (35) produced enough furfural ten years later to enable him to determine its physical constants and formula. Stenhouse used sawdust and oatmeal as raw materials for this production. Later (36) he produced larger quantities by steam distilling wheat bran with dilute sulfuric acid in 30 gallon earthenware Woulf bottles.

Table 2. Properties of loess samples

Sample numbers	55-1	20-2	20-2II
Sand (2.0 to 0.074 mm), per cent	0.5	1.4	0.7
Silt (0.074 to 0.005 mm), per cent	91.1	78.8	78.9
Clay (below 0.002 mm), per cent	7.4	15.1	17.8
Colloidal clay (below 0.001 mm), per cent	6.5	14.5	17.5
Liquid limit, per cent	29.6	30.8	33.2
Plastic limit, per cent	27.3	24.6	24.0
Plasticity index, per cent	2.3	6.2	9.2
pH	8.0	8.7	7.8
Cat. Ex. Cap. (m.e./100 gm)	10.0	13.4	12.6
Carbonates, per cent	7.6	10.2	6.9
Organic matter, per cent	0.21	0.17	0.19
Textural Classification (B.P.R. System)[1]	silty loam	silty loam	silty clay loam
Engineering Classification (AASHO)	A-4(8)	A-4(8)	A-4(8)

[1]Textural classification is based upon the Bureau of Public Roads System except that sand and silt are separated by the No. 200 sieve

Table 2. (Continued)

Sample number	26-1	36-1	44A-1
Sand (2.0 to 0.074 mm), per cent	0.5	0.4	0.2
Silt (0.074 to 0.005 mm), per cent	74.8	69.6	58.9
Clay (below 0.002 mm), per cent	21.7	26.3	30.6
Colloidal clay (below 0.001 mm), per cent	21.4	25.0	29.4
Liquid limit, per cent	34.7	39.0	53.1
Plastic limit, per cent	24.0	25.6	25.7
Plasticity index, per cent	10.7	13.4	27.4
pH	7.9	6.5	6.2
Cat. Ex. Cap. (m.e./100 gm)	15.3	19.6	23.1
Carbonates, per cent	6.4	0.7	0.8
Organic matter, per cent	0.25	0.14	0.52
Textural Classification (B.P.R. System)[1]	silty clay loam	silty clay	silty clay
Engineering Classification (AASHO)	A-6(8)	A-6(9)	A-7-6(19)

[1] Textural classification is based upon the Bureau of Public Roads System except that sand and silt are separated by the No. 200 sieve

Table 2. (Continued)

Sample number	46-1	503-2
Sand (2.0 to 0.074 mm), per cent	0.4	2.0
Silt (0.074 to 0.005 mm), per cent	67.9	55.2
Clay (below 0.002 mm), per cent	26.3	37.0
Colloidal clay (below 0.001 mm), per cent	24.2	34.5
Liquid limit, per cent	54.7	56.7
Plastic limit, per cent	22.0	26.4
Plasticity index, per cent	32.7	30.3
pH	5.9	6.4
Cat. Ex. Cap. (m.e./100 gm)	23.6	28.1
Carbonates, per cent	0.9	0.8
Organic matter, per cent	0.23	0.72
Textural Classification (B.P.R. System)[1]	silty clay	clay
Engineering Classification (AASHO)	A-7-6(19)	A-7-6(19)

[1]Textural classification is based upon the Bureau of Public Roads System except that sand and silt are separated by the No. 200 sieve

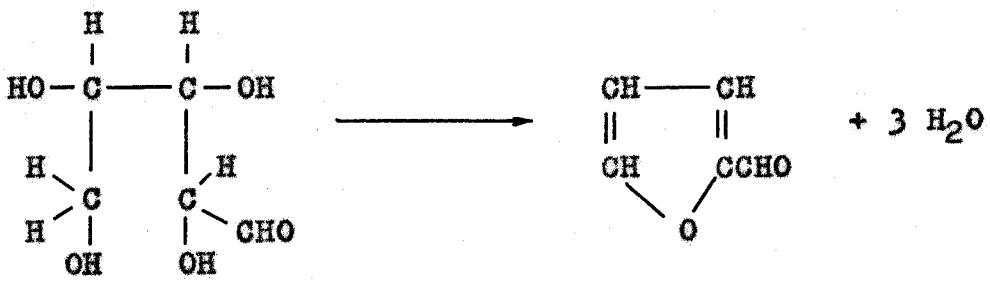
The name "furfural" was suggested by Fownes in 1845 when he produced it from bran. The name was derived from the Latin word "furfur" which means scale, scurf, dandruff or bran. Later tests showed the product to be an aldehyde and it was then called furfur-aldehyde. The chemical is now commonly called furfural, the suffix "al" referring to the aldehyde group attached to the furan ring.

Other names of furfural are 2-furaldehyde, 2-furancarbonal, 2-furancarboxaldehyde, fural, furole, furaldehyde, pyromucic aldehyde and artificial oil of ants. The International Union of Chemistry has approved the name 2-furancarbonal. Regardless of all these names furfural has endured and is by far the most common name in the literature and in industrial usage.

The two isomeric aldopentoses, l(+)-arabinose and d(-)-xylose, are formed by the hydrolysis of polysaccharides of high molecular weight known as pentosans. The pentosans and some similar compounds which yield mannose and galactose on hydrolysis are known as hemicelluloses. Hemicelluloses are widely distributed in plants and are particularly associated with cellulose in cell walls.

Hexoses are all sugars with six carbon atoms and the pentoses are sugars having five carbon atoms. The name aldohexose indicates a six-carbon sugar with an aldehydic group. Similarly the name aldopentose indicates a five-carbon

sugar with an aldehydic group. Aldopentoses and aldohexoses are very similar in most of their reactions but may be differentiated by the action of hot hydrochloric or sulfuric acid. Only the pentoses form the volatile aldehyde known as furfural as illustrated by the following dehydration of an aldopentose which is the basis for furfural production:



Briefly, furfural is produced by the hydrolysis of a pentosan to a pentose followed by dehydration of the pentose to form the aldehydic furan ring. All the aldopentoses can be converted into furfural by the action of hot dilute sulfuric acid since this reaction is not dependent on stereochemical configuration.

Stone and Lotz (37) in 1891 distilled corncobs with hydrochloric acid and recorded a yield of 22.12 per cent of furfural, based on the dry weight of raw materials. Research on the composition of corncobs at Iowa State College (38) in 1917 indicated a furfural content of 23.3 per cent. Work was started in 1920 on the production of furfural from corncobs in the Chemical Engineering Laboratory (2).

LaForge and Hudson (22, 24) and Monroe (28) of the

Bureau of Chemistry of the United States Department of Agriculture contributed important work in a search for industrial uses for corncobs. A semi-commercial unit was put into operation by the Bureau of Chemistry in 1922 (23). The yield obtained was 6 per cent of the weight of the cobs. Yields up to 11.7 per cent were secured at Iowa State College by increasing the reaction temperature (17).

Subsequent work at Iowa State College (13) showed a yield of 12.5 per cent furfural, or about 80 per cent of theoretical, could be obtained from sugar cane bagasse treated with dilute sulfuric acid and steamed at atmospheric pressure with super-heated steam at 180° C.

Modern day furfural manufacture consists essentially of seven main steps: 1. Pressure cooking of the raw material with dilute acid, 2. condensation of cooker vapors, 3. azeotropic distillation of furfural, 4. condensation of two layers and decantation of water layer, 5. distillation of water layer to recover methanol, 6. drying of furfural, 7. decoloring and filtration.

Ground oat hulls, cottonseed hulls, ground corncobs, or similar material is premixed with dilute sulfuric acid and charged into large spherical rotary digestors. Under 70 pounds of steam the pentosans are hydrolyzed to pentoses, which then split out water to form furfural. Side reactions produce smaller quantities of acetic acid, methanol and other

compounds.

Residue from the digester is flash-dried and pulverized and then used as a fuel to produce steam or is sold as a fertilizer conditioner. Vapors of the reaction products are carried out of the digester by steam and are passed into a stripping column. Furfural is azeotropically distilled and after condensation is run into a decanter. The top water layer is run into a column to recover methanol and acetaldhyde and the column bottoms are returned to the stripping column.

The bottom layer of furfural is dried by stripping off the water and methanol in a dehydrating column. After cooling, the furfural is passed through a pressure filter to give a technical grade of furfural of 99.5 per cent purity. A refined special grade of furfural is made by redistillation and decolorization of the technical grade. An oxidation inhibitor is generally added to minimize darkening when subjected to light and aging.

Material requirements for the production of one ton of furfural are given in Industrial Chemicals (12) as 15,000 pounds of oat hulls, 225 pounds of 100 per cent sulfuric acid and 40,000 pounds of steam.

Quaker Oats Company of Chicago is the major producer of furfural. They operate three plants, one in Cedar Rapids, Iowa, one in Memphis, Tennessee and one in Omaha, Nebraska.

The first commercial plant was constructed in Cedar Rapids, Iowa by Quaker Oats for the production of furfural from oat hulls. The plant used the acid hydrolysis method previously used on corncobs and started operating in 1922.

The newest and largest plant in the world began operation at Memphis, Tennessee in July 1943. The plant was operated for the government by a subsidiary of the Quaker Oats company until November 1946. It was then purchased by Quaker Oats and now operates as one of its units.

The total present day production of furfural is in the neighborhood of 50,000,000 pounds per year. Procurement, handling and storage of thousands of tons per month of raw material must be done under the most economical conditions. The Memphis plant used cottonseed hulls primarily but has used corncobs. Various raw materials containing pentosans may be used. Whether an industrial by-product such as oat hulls and cottonseed hulls or a farm residue such as corncobs is used depends on the economic situation. Generally the cost of corn cob collection, even from elevators, is such that industrial by-products are cheaper raw materials.

Tremendous production of furfural and ethyl alcohol has been proclaimed the panacea for all farm problems but the cost of collection of agricultural residues has prohibited such a program. The annual crop of corn cobs is about 16,000,000 tons or enough to yield 3,000,000,000 pounds of

furfural. About five years ago the U. S. Department of Agriculture initiated an extensive pilot plant study on the conversion of agricultural residues to furfural and alcohol.

Uses of furfural

Pure freshly distilled furfural is a transparent liquid which gradually darkens, particularly if exposed to light and air. Technical furfural which has stood for some time may be dark brown.

The physical properties of furfural are important in such applications as selective solvent refining of petroleum, rosin and other products. In some applications both the physical properties of furfural as a solvent and its subsequent reactivity are the basis for its use. An example is its function as a reactive solvent in making resinoid bonded abrasive wheels.

Furfural is industrially important in the manufacture of phenol-furfural resins, various special types of resins, a chemical intermediate in the manufacture of nylon, as a preservative for wood and leather, and as a selective solvent in the removal of sludge-forming materials from lubricating oils.

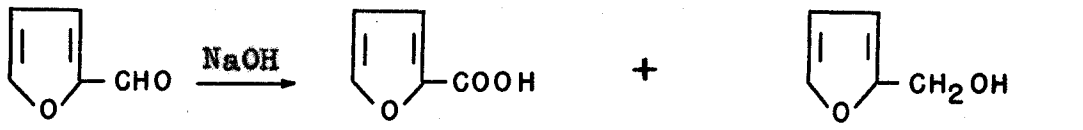
Table 3. Physical constants of furfural (32)

Molecular weight	96.08
Melting point, ° C.	-36.5
Boiling point, ° C.	161.7
Flash point (open cup), ° C.	56.8
Viscosity of 25° C., centipoises	1.49
38° C.	1.35
54° C.	1.09
99° C.	0.68
Lower explosive limit at 125° C., vol. % in air	2.1
Surface tension at 20° C., dunes/cm	49
Heat of vaporization at 160.6° C. gm cal/gm mol	10,321
Dielectric constant at 25° C.	38
Refractive index 20/D	1.5261
Heat of combustion, kg cal/gm mol	560.1
Specific gravity 20°/4° C.	1.1598
Solubility in water (wt. % at 20° C.)	8.3
alcohol	infinite
ether	infinite
Ignition temperature, ° C.	315-357

Reactions of furfural

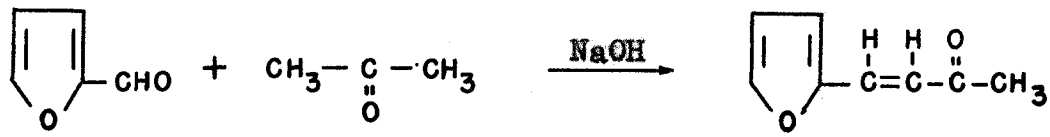
Furfural closely resembles benzaldehyde in chemical properties. This similarity is illustrated by the following reactions (3):

Cannizaro reaction

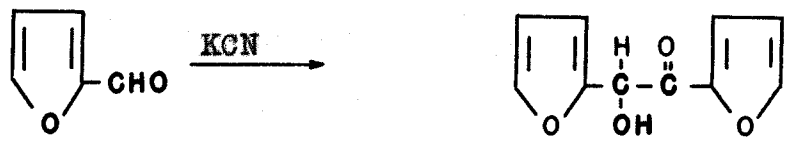


Furoic acid Furfural alcohol

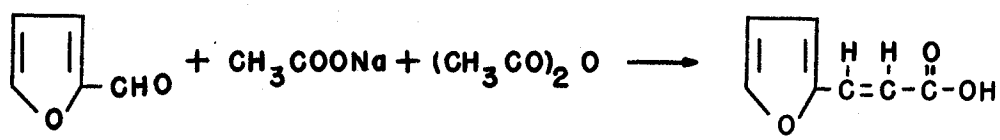
Claisen Condensation



Benzoin type of condensation

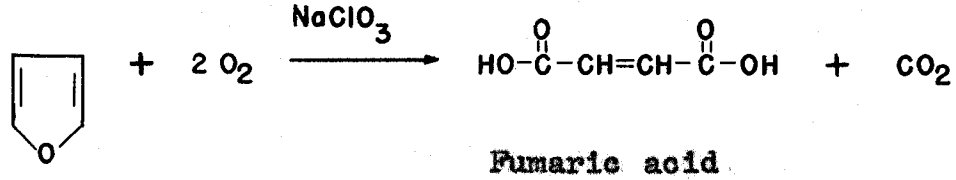


Perkin reaction



This comparison could be carried much further. Furoin can be oxidized to the diketone, furil, which can then be converted into furilic acid by action of alkali.

Mild oxidation converts furfural into furoic acid. Strong oxidation with sodium chlorate solution breaks the furan ring and produces fumaric acid.



Fumaric acid

Furfural also reacts with a variety of other chemicals to form synthetic resins. A few examples of chemicals that furfural reacts with to form resins are phenol, urea, lignin-cellulose, ketones, aniline, and sulfonamides. The reaction of furfural with aniline is treated elsewhere in this dissertation.

Aniline

Aromatic amines are derivatives of ammonia in which one or more of the hydrogen atoms are replaced by one or more aromatic radicals. They may be divided into three classes: primary, secondary and tertiary amines. These class names are descriptive of the number of hydrogen atoms that have been replaced by the aromatic radical. Thus aniline is a primary aromatic amine.

Aniline is the parent aromatic amine to which all other compounds in this organic family are related. It has therefore been used as the basic classical example in the study of the chemical behavior of the aromatic amines. There has been a great amount of research and writing done concerning the chemical characteristics and behavior of aniline.

Aniline was first obtained in 1826 by Unverdorben (40) through the destructive distillation of indigo with lime. The name "aniline" is derived from the Spanish word "anil" which means indigo. Zinin in 1842 discovered a method of convenient preparation in which nitrobenzene is reduced to aniline. He called the substance "benzidam" because he recognized that it was related to both benzene and ammonia.

Aniline, like furfural, is known by many names among which are: aniline oil, phenylamine, aminobenzene, aminophen, benzidam and benzidiam. The compound is most commonly called aniline except in medical and pharmaceutical circles where it is known as aniline oil.

Aniline is manufactured by the reduction of nitrobenzene, ammonolysis of chlorobenzen and vapor-phase hydrogenation of nitrobenzene. The last process is not widely used although a number of patents have been granted. About 75 per cent of production is performed by the old batch method of reduction of nitrobenzene. Numerous variations of aniline recovery are used. Steam distillation of the entire charge is costly and has been largely superseded by mechanical separation of the aniline layer and steam sparging of the remaining slurry. Yield is very important since raw materials represent nearly 75 per cent of the total product cost. An economic balance must therefore be made between aniline recovery and steam costs. The continuous process of ammonolysis of chloroben-zene is competitive with the batch process and offers natural

operating economics.

The batch process is described here because of its simplicity and predominance. Crude nitrobenzene is charged into a reactor fitted with a reflux condenser. Cast-iron borings or powder, water and hydrochloric acid catalyst are gradually added to the nitrobenzene. Ten to 20 per cent of the iron is usually added at the beginning and the mixture is then steam heated to the reflux temperature of 200 degrees Centigrade. The remaining iron is added over a period of time at a rate determined by the proper temperature-pressure balance. The acid and iron react to form catalytically active iron salts. Subsequent runs may utilize the aniline-hydrochloric acid mother liquor as a source of the catalyst and reaction water.

About 10 hours of reaction time is required for a 5000 pound charge, at the end of which the aniline is separated from the solid iron oxide-iron hydroxide sludge by steam distillation, vacuum distillation, filtration, centrifugation or syphoning.

The water-aniline mixture from the reducer is run to a separator where the heavier aniline separates to the bottom and is withdrawn. The top water layer containing 3 to 5 per cent aniline is partially distilled until the aniline content is quite low. The remaining aniline water is returned for subsequent runs.

Aniline from the separator and from the decanter is

united and vacuum-distilled to yield purified aniline. The yield based on the nitrobenzene charge is approximately 95 per cent by weight. By way of comparison the yield of aniline from the chlorobenzene process is 85 to 90 per cent by weight of chlorobenzene (8).

Uses of aniline

The dye manufacturing industry has for many years used the major production of aniline. Wartime demands for aniline, as an intermediate in the manufacture of diphenylamine for smokeless powder and in the manufacture of tetryl, were high. The manufacture of synthetic rubber additives such as hydroquinone and cyclohexylamine also required large quantities of aniline during World War II. This latter market remains to some degree today. Aniline is also used in the manufacture of medicinals, synthetic resins, varnishes, and perfumes.

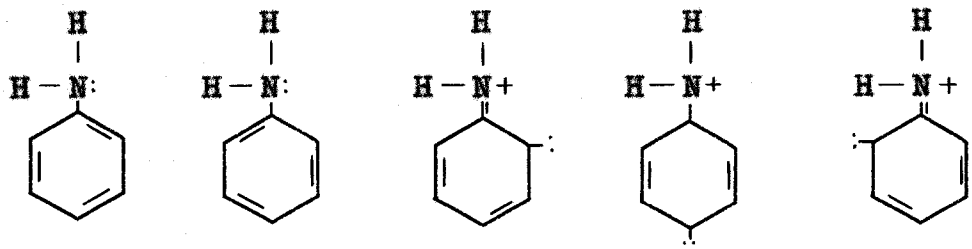
Reactions of aniline

A study of aniline is a direct approach to the understanding of the chemical behavior of the aromatic amines. For this reason there has been a large amount of research done on aniline and most organic text books list the reactions in detail.

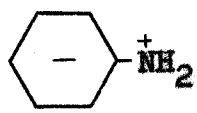
Table 4. Physical constants of aniline (12, 27)

Molecular weight	93.12
Specific gravity	1.022 20/20
Melting point	-6° C.
Boiling point	184-186° C.
Flash point	70-76° C.
Ignition temperature	1000° C.
Vapor density (air = 1)	3.22
Weight per gallon (20° C.)	8.52 lbs.
Water solubility (18° C.)	3.6 g per 100 ml.
Organic solvents	Alcohol Chloroform Benzene
Dipole moment	1.56 D

The average structure of the aniline molecule is intermediate between the extremes shown in the following resonance forms:



Generalized form



The dipole moment of aniline is 1.56 debye units as opposed to 1.03 debye units for hydrochloric acid. Dipole moments are of the order of 10^{-18} electrostatic units which is then called "one debye" in honor of Professor Peter Debye for his extensive work on polar molecules.

A certain degree of basicity may be expected from aniline because there is a tendency for a pair of electrons to be unshared at the nitrogen atom. This basicity is less than that of ammonia because of the shift of electrons toward the ring. The increased electron density on the ring accounts for the ease of substitution, for ortho and para orientation and for the oxidation of aniline to colored products on exposure to air.

Aniline may accept a proton from water to form phenylammonium hydroxide which then ionizes to form a weak base. A

water solution of aniline is nearly neutral to litmus but it is sufficiently basic to precipitate slightly soluble metallic hydroxides. It also forms salts with acids which in turn may form double salts.

Aniline reacts with benzoyl chloride giving benzanilide and with ethylchlorocarbonate to form phenylurethane. These reactions are illustrative of the ability of aniline to donate electrons from the nitrogen atom to an external, carbon atom. The nitrogen atom of aniline has an unshared pair of electrons which provide the key to most of the reactions of aniline. The nitrogen is an electron donor and the proton is an electron acceptor. The nitrogen atom of aniline donates electrons to such a carbon atom and a coordination compound is formed.

Aniline reacts with aldehydes to form a group of compounds that are known as the "Schiff" bases. These compounds are named in honor of Dr. Hugo Schiff (1834-1915) who was professor of chemistry in Florence, Italy. The production of benzalaniline is a typical example.

$$C_6H_5 - NH_2 + C_6H_5 CHO \longrightarrow C_6H_5CH = N\text{-}C_6H_5 + H_2O$$

Alkylation of aniline is easily accomplished by means of a polarized carbon-halogen bond. The carbon atom of an alkyl halide attracts electrons and is therefore well suited to react with the unshared pair of electrons on the nitrogen atom of aniline.

Resonance forms of aniline indicate that ortho-para orientation in ring substitution is to be expected in aniline. This prediction is borne out in the usual behavior of aniline. When a few drops of aniline are shaken with bromine water, a precipitate of 2,4,6,-tribromoaniline is formed almost instantaneously. Sulfonation, arsenation and nitration of aniline as well as bromination may be accomplished with ring substitution occurring in either or both the ortho and para positions.

The high electron density of the aniline ring makes oxidation (electron removal) very easy. Aniline acquires a dark red color upon exposure to air as a result of atmospheric oxidation. The extent of oxidation under these conditions is very slight. If required, aniline may be distilled back to its original nearly colorless form since the oxidized material is nonvolatile.

The aniline-furfural reaction

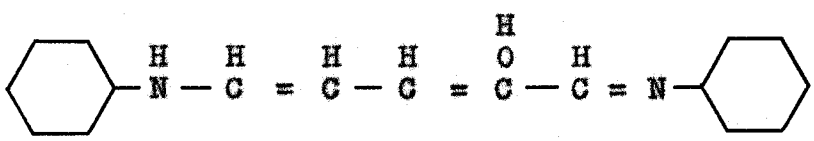
Since very little work has been done on the analysis of aniline-furfural polymer structure, only the theoretical possibilities of the reaction mechanism can be presented. The following discussion is intended to point out that certain structures are possible and consistent with results of stabilization research.

Gieseking (18) has commented as follows:

> Furfural enters into many different types of reactions. One wonders if anyone is able to comprehend all of the possibilities and all of the conditions that might tend to alter the courses of the reaction. We can be sure, however, that some of the products of the reaction between furfural and aniline will be large organic cations.

Furfural alone polymerizes slowly into resinous materials on standing and also forms resins when reacted with a number of organic chemicals. Mains and Phillips (26) have reported the production of a synthetic resin by reacting equal parts of aniline and furfural. Sweeney, Arnold, and Long (39) reported a resin of 6 per cent by weight of aniline in furfural produced a flexural strength of 500 pounds per square inch after seven days curing at room temperature.

Winterkorn (43) presents an excellent discussion of the history and the present knowledge of the aniline-furfural reaction. He has also investigated the chemical concepts of the reaction and has supported the structure proposed by Zincke and Muhlhausen in 1905. The structure, in which the furan ring is ruptured, is as follows:



Present day information on this subject is scarce and does not permit a decisive conclusion as to the nature and structure of aniline-furfural resins. The 2:1 aniline-furfural resin is probably composed, like many other resins,

of one main product mixed with a number of intermediate products.

Toxicology of aniline and furfural

The toxicity of aniline has been studied in considerable detail because of its industrial importance and uses. Since there is a possible engineering use for aniline, it is felt that a discussion of this subject is necessary to acquaint engineers with the severity of aniline poisoning.

According to Osol and Farrar (31) the symptoms produced by the inhalation or ingestion of aniline are headache, nausea, prostration, giddiness, mental confusion and violent neuralgic pains. If the dose has been large enough these symptoms are followed by cyanosis, excessive perspiration, loss of reflexes and voluntary movement, hurried weak pulse, rapid or irregular respiration, hemoglobinuria and coma with dilation of the pupils. Sufficiently long survival of a large dose of poisoning produces jaundice with a great increase in the biliary pigment of the skin.

Subacute cases (14) of aniline poisoning may show attack of the liver and kidneys with the production of diarrhea and jaundice. The urine may be dark from oxidation products, erythrocytes and hematoporphyrin. The illness is often prolonged from five to six weeks in non-fatal cases. Characteristic postmortem findings in acute fatal cases are

brownish discoloration of the blood and tissues and a strong odor of aniline in the various organs.

Cases of chronic poisoning develop anemia, skin eruptions, nervous symptoms, and amblyopia. Chronic cases lasting a number of years occasionally develop bladder carcinomas as a result of continuous irritation of that organ. Aniline workers exhibit a high incidence of papillomas and carcinomas of the bladder. Development may come several years after exposure. This high incidence in aniline and synthetic dye workers has been reported by Gehrmann of the United States and by many German authors. Schwartz, Tulipan and Peck (34) report that there is a general agreement that benzidene and beta napthylamine are the chief carcinogenic agents in these factories. Various writers have named aniline, rhodamine, fuschin and alizarine as causes of cancer but have not proven these statements.

Furfural has very mild toxic effects compared to those of aniline. Five grain daily doses (41) to dogs and rabbits showed little toxic effects while one gram daily doses proved fatal to fowl. Fairhall's Industrial Toxicology (11) states that 280 parts per million of furfural caused only slight irritation to the mucous membrane of lower animals. Furfural is less apt to produce contaminated atmospheres than aniline because a higher concentration is required for toxic effects. Continued exposure to furfural can produce chronic effects,

so unnecessary exposure should be avoided.

The Merck Index (27) gives the toxicity as about one-third that of formaldehyde. Furfural causes lacrimation, inflammation of the eyes, irritation in the throat and headache. Symptoms of chronic poisoning are nervous disturbances, photosensitivity, and disturbance of vision.

First aid and treatment of aniline poisoning

Goodman and Gilman (15) state that if aniline vapors are inhaled the victim should be removed immediately to fresh air. Aniline spilled on the skin should be washed off promptly. Large amounts of water may be used but alcohol or ether is preferable to water since aniline is very soluble in these solvents. Treatment is the same as for acetanilid poisoning. Special emphasis should be placed on shock therapy, cardiovascular system support and correction of the acute anemia with oxygen inhalation, methylene blue or ascorbic acid administration, and blood transfusion if necessary.

Gonzales et al (14) recommends removal of the victim from the source of exposure and washing of the stomach if aniline has been swallowed. Covering the victim with blankets and administration of oxygen may be desirable. Condition of the blood may also indicate that infusions and transfusions are necessary.

Osol and Farrar (31) state that ingestion of as little as 0.25 cc. of aniline may produce symptoms of poisoning. Recovery has followed ingestion of 75 cc., on the other hand ingestion of 25 cc. has proven fatal. The maximum allowable vapor concentration is 5 parts per million (27).

Methods of Testing

Since little is known about the effects of many variables that influence the final stability of a soil-aniline-furfural system the necessity to investigate some of these variables is immediately apparent. The most important of all variables appears to be the amount of water used to obtain maximum density. This is a well established fact in mechanical stabilization. However, aniline-furfural stabilization shows some peculiar characteristics of moisture sensitivity both in mixing and in compaction.

Mainfort (25) has reported some data on moisture-density relationships of soil-aniline-furfural systems in which he found that this relationship for most soils is somewhat modified by the addition of certain chemicals. Therefore, each soil with varying percentages of aniline-furfural has been investigated over a range of moisture content sufficiently large to clearly define optimum conditions. This also defines the maximum density possible with any specified compactive effort.

Displacement of maximum mechanical stability from maximum density was studied by compression testing all specimens molded at the various moisture contents. Once an optimum moisture condition was established, for a given system, it was employed in any further stability studies.

The density of a stabilized soil may be expressed either as the weight of a soil contained per cubic foot of material or as the weight of soil plus stabilizer per cubic foot of material. The former definition will be referred to as dry density throughout this dissertation while the latter will be known as the stable density. Wet density refers to the weight of soil plus water per cubic foot of material and does not include the weight of aniline-furfural. Wet stable density does include the weight of aniline-furfural in addition to that of the water contained in a cubic foot of material.

Specimen molding

Samples were molded in cylinders two inches high by two inches in diameter in a free cylinder compaction apparatus. The apparatus is shown in Figure 2. Experience has shown that an equal number of blows on both ends of a specimen produces the most uniform density throughout the specimen. The ability of this apparatus to produce near standard Proctor densities is shown in Table 5.

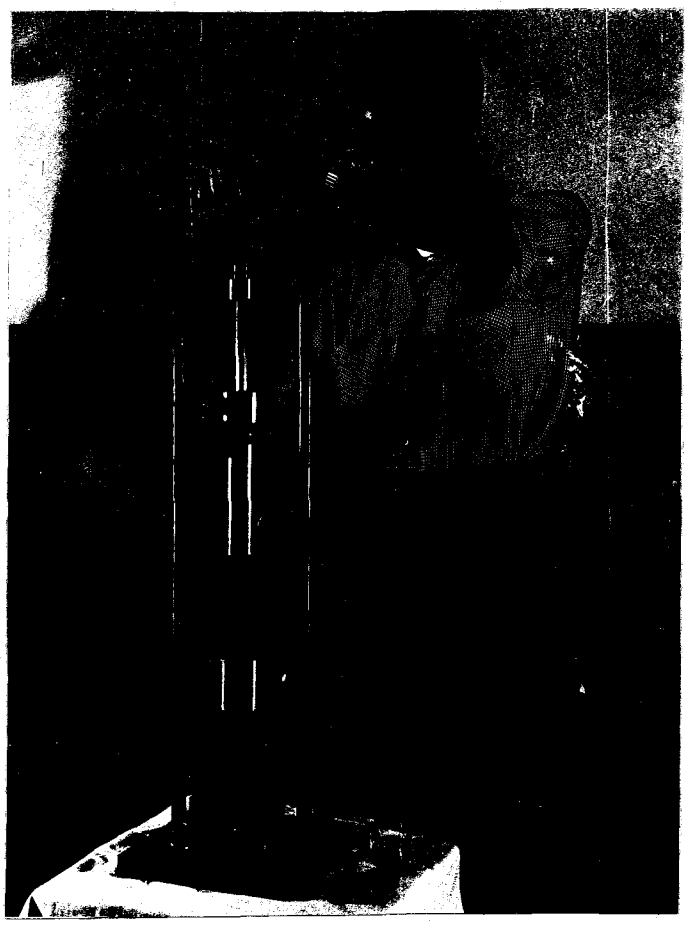


Figure 2. 2 x 2 free cylinder compaction apparatus

Table 5. Comparison of standard Proctor compaction and compaction by the 2 x 2 compaction apparatus

Soil	Standard Proctor		2 x 2 Apparatus	
	Optimum moisture content per cent	Maximum dry density lb. per cu.ft.	Optimum moisture content per cent	Maximum dry density lb. per cu.ft.
55-1	19.0	103.0	21.1	101.0
20-2-II	18.1	107.4	19.2	106.1
26-1	18.1	109.2	18.5	109.2
36-1	20.0	105.2	19.6	106.4
46-1	21.5	102.7	21.6	103.9
503-2	23.3	97.3	24.5	99.8

The compaction hammer weighs five pounds and is dropped from a height of one foot above the compaction head. Each specimen was molded by pouring the mixture of soil, water, and chemicals into the molding cylinder and dropping the hammer a specific number of times on the soil mixture. The cylinder containing the partially compacted specimen was then inverted and the compaction effort repeated on what was the bottom end of the specimen. The molded specimen was then extruded, weighed to the nearest 0.1 gram, and its height measured to the nearest 0.001 inch.

A total of six 2 x 2 specimens were molded from each batch and set aside for curing. The height of all specimens

was kept near 2 inches (plus or minus 0.05 inch). A little experience is required to find the correct weight of wet mixture to create a molded specimen within these height limits. Usually three samples were used for wet testing and three for dry testing unless a specimen was ruined in handling. All results given are averages of three specimens except in very few cases where the averages are of two specimens.

Determination of moisture content

The moisture content of soil refers to the total amount of water held in the soil either as free water, as capillary water in the soil pores, or as absorbed water films. Moisture content is defined as the ratio of the weight of water contained in the soil to the weight of the dry soil. It is expressed as a percentage and is determined by heating the sample in an oven at a temperature between 100 and 110 degrees Centigrade. The difference between the weight of the sample before drying and the weight of the sample after drying is taken as the amount of moisture contained in the soil.

Moisture determination in samples containing unreacted aniline-furfural presents a difficult problem since aniline and furfural are both volatile. Some loss of these chemicals occurs along with the normal loss of water although the

resin forming reaction begins immediately on contact between the aniline and furfural. The rate of resin formation is dependent upon many factors including temperature and catalysis while the rate of volatilization is dependent mainly on temperature and the amount of unreacted material present. Research done on this problem has indicated that the loss of unreacted chemicals is also dependent upon the amount of water present at the time of mixing.

The weight of the material after oven-drying includes both the original amount of soil and the residual aniline and furfural that have reacted to form the non-volatile resin. Since varying percentages of resin were studied all moisture contents for molding purposes were computed as a percentage of the oven-dry soil. This places the moisture contents at the time of molding on a common basis and permits a comparison of all mixtures including those composed of only soil and water.

After curing most of the original mix water has been lost through evaporation and the residue is soil, hygroscopic moisture and aniline-furfural resin. Moisture is absorbed when treated specimens are immersed or otherwise brought into contact with water or water vapor. Since this moisture is apparently absorbed by both soil grains and the stabilizing resin the percentage absorption is based on the combined weights of the soil and the resin.

The moisture content of specimens molded from a prepared batch may be determined by adding the hygroscopic moisture of the soil used and the amount of water incorporated into the mixture. This method of moisture determination is subject to the errors of evaporation during mixing, evaporation during the process of molding, and the limitations of quantitative measurements prior to mixing. A correction was introduced to compensate for evaporation loss during mixing by adding a predetermined amount of extra water to the mass before mixing. Evaporation during molding was kept at a minimum by covering the mixing bowl containing the batch of soil, water, and aniline-furfural with a water saturated cloth. This keeps the partial pressure of the water vapor in the atmosphere above the mixture at a maximum and evaporation from the mixture at a minimum. Errors due to volumetric apportionment of fluids are easily kept within limits of 1/2 a gram. Since the magnitude of the soil mass is over 1000 grams the error due to volumetric measurement is less than 0.05 per cent of the soil.

As a check on the accuracy of the aforementioned method for moisture determination some tests were made in which small individual samples of 2:1 aniline furfural-water-soil systems were oven dried at 100-110 degrees Centigrade. The soil was first weighed in a small aluminum weighing can after which furfural was added and mixed into the soil. The can

and contents were again weighed to determine, by difference, the amount of furfural added. Water was then added and mixed with the soil and furfural. The can and total contents were again weighed. Finally aniline was added and mixed into the system, the total amount was again weighed and placed in an oven for 24 hours. All of these weighings, together with a separate determination of hygroscopic moisture in the soil, permitted an accurate material balance to be made. The oven-dried sample was weighed and the amount of aniline-furfural lost was determined.

A number of similar samples were made, varying the amount of aniline-furfural and the amount of water in each sample. It was found that a plot of the percentage of the aniline-furfural lost in drying versus the weight ratio of initial amount of water to initial amount of aniline-furfural was very close to a straight line with a slope of one and an intercept of 17. The equation of this line permits the derivation of a moisture content equation dependent only on the variables of total loss after oven-drying and the total residue after oven-drying. The method of derivation of this equation can be found in the discussion of results.

Ogilvie (29) has also made a similar study and found that the moisture may be determined, without appreciable error, by the total volatiles lost expressed as a percentage of the total residue. This was subject to the condition that

the moisture sample be held in a covered can for 30 minutes before placing in the oven. The 30 minute period appears to be sufficient for the aniline and furfural to react to a degree that minimizes losses in the oven or at least makes the losses consistent. The author's method requires samples to be placed in the oven immediately.

Preparation of mixtures

Air-dried soil with 100 per cent passing a No. 10 sieve was weighed into a mixing bowl to provide 1200 grams on an oven-dry basis. The entire quantity of furfural and about one half of the distilled water required for the mixture was added and folded into the soil with a mixing spoon. This initial hand mixing is required to dampen the soil enough to prevent dusting. The balance of the distilled water was added and mixed with the soil and furfural with a Hobart Model C-100 mixer at low speed. After mixing for one minute the mixer was stopped and the soil-water-furfural mixture was hand mixed for another minute. The aniline was then added and the mixer allowed to run for two minutes after which the mixer was again stopped for another one minute period of hand mixing. Finally mixing was completed with another full minute of machine mixing. The hand mixing was found to be necessary because of the tendency for the mixture to pile up in the bottom of the bowl. It was found that soils with

higher clay percentages were better mixed at a medium speed. The high speed throws some of the soil completely out of the bowl and therefore was not used.

The ratio of aniline to furfural was kept on a 2:1 molar basis since all prior and present research indicates that these are the best stoichiometric quantities for the formation of the optimum quality aniline-furfural resin. The chemicals were added volumetrically with an accuracy of 0.1 milliliter which is under 1 per cent based on total chemicals added. The volumes were computed from the specific gravity values given in the tables of physical properties. Desired percentages of chemical composition were produced by addition of the appropriate volumes of aniline and furfural.

The six minute mixing period was selected on the basis of a visual inspection of the condition and color of the material. The order of mixing is discussed later in this dissertation.

Samples for any one study were molded the same day in order to insure a curing period of identical atmospheric conditions for all specimens to be compared. Since the kinetics of the reaction appear to be somewhat effected by the rate of moisture loss from the samples it is important that the curing conditions for a comparative study be identical for all samples involved.

Catalysts studied were introduced by means of the mix

water. The catalyst was weighed and introduced into a graduated cylinder and the volume brought up to the desired level to produce optimum moisture conditions. This solution was introduced into the mixer in the same manner as was distilled water.

Ratio study

A study of the effects of the ratio of aniline to furfural was made in which this ratio was varied from 1:4 to 3:1. The total amount of aniline and furfural was held constant at 5 per cent and mixed with soil 20-2 to have a common basis for comparison. The wet and dry compressive strengths were determined along with the total volatile loss and the moisture absorption after 24 hours immersion in distilled water.

Study of order of mixing

Batches of soil in which all possible combinations of the order in which the chemicals and the water were introduced were mixed. The resulting mixtures were molded and cured for 10 days and then tested for dry strength, wet strength, deformation at failure when tested dry, deformation at failure when wet, water absorption, loss of volatiles, shrinkage, and swelling on immersion. The results were tabulated and an arbitrary value of 10 was assigned to the

best performance in each test, 9 to the second best, 8 to the third, and so on. The first five tests were used as evaluation criteria as they were considered the most important. The last three did not vary significantly so they were not considered. The results were tabulated in order of highest value first.

Density study

Early in this study of aniline-furfural stabilization it was discovered that molding samples by drop hammer compaction, on one end of the sample only, produced a phenomenon which has been termed cupping. A convex lens of soil of approximately the same diameter as the sample either fell from the bottom of the sample after molding, appeared as a secondary failure plane after compression testing, or appeared as a failure plane after 24 hours immersion in water. Attempts at a remedy of this situation were made and it was finally found that cupping can be eliminated by compacting the specimen with an equal number of blows on both ends of the specimen.

Compaction on both ends of a specimen raised the question of the variation in density within the specimen. This was studied by molding specimens, stabilized with 11 per cent aniline-furfural, first with 10 blows on one end and second with 15 blows on each end. These specimens were cured for 10

days and then sawed into quarters with a hack saw. The density of each quarter was determined by weighing the quarter and then finding its volume by the method of mercury displacement that is used in determining shrinkage limits.

The densities obtained by an equal number of blows were compared to those obtained by the use of a Harvard miniature compactor. The comparison was made with soils 20-2 and 44A-1 stabilized with 0, 5, and 11 per cent aniline-furfural. Three, five, seven, and nine blows on each end were used and a moisture-density curve drawn for each energy level of compaction.

Drying study

Batches of soil 20-2 stabilized with varying percentages of aniline-furfural were molded at Proctor densities. Each specimen was weighed daily until the weight remained constant or nearly so. The specimen was weighed again five days later to check the constant weight and the losses were plotted against time for all percentages of aniline-furfural. Some specimens were then dried in an oven to determine residual or hygroscopic moisture. All specimens were tested in unconfined compression after the final weighing in the drying experiment. Some specimens were immersed for 24 hours in distilled water and tested. Total deformation at failure was determined on all specimens tested for unconfined compressive

strength.

Curing study

Specimens of soil 20-2 were molded the same day with 5 and 11 per cent aniline-furfural at Proctor density and allowed to air cure. After a definite curing period three samples were tested in unconfined compression while three more were immersed before being tested in unconfined compression. The immersed samples were also weighed after immersion to determine the amount of absorption. Several specimens of each percentage were kept in the laboratory for 22 months before testing.

Physical measurement of specimens

Soil used in mixing was weighed on a Fischer direct reading balance with a sensitivity of one gram. Since all batches were mixed from 1200 grams of soil the error of weighing was less than one-tenth of one per cent. Specimens were weighed with triple beam balances sensitive to 0.1 gram, again keeping the error of weighing below 0.1 per cent. Moisture determinations were made with torsion balances sensitive to 0.01 gram.

Heights and diameters were measured with Ames dials accurate to 0.001 inch.

Unconfined compression testing

Unconfined compression tests were made with a Riehle 60,000 pound capacity hydraulic testing machine. Since the dial was calibrated in 20 pound increments, all data was read to the nearest 10 pounds. The compressive load was applied at a rate of 0.1 inch deformation per minute. The maximum load causing a specimen to fail was recorded.

Except as otherwise stated in specific studies the testing of specimens was performed as proposed by Davidson (18, p. 80). Heights and weights of all specimens were recorded after a ten day curing period. Even numbered specimens were immersed in distilled water for 24 hours at room temperature. Odd numbered specimens were tested for unconfined compressive strength immediately following their physical measurements and the results reported as dry strength.

The immersed specimens were blotted dry with paper towels, measured, and weighed after 24 hours immersion. The specimens were then reimmersed to avoid excess drying before compression testing. Individual specimens were removed from the immersion bath and placed in the testing machine dripping wet just before testing. Results are reported as wet strength. All expansion and absorption data were calculated on the basis of the stabilized weight and dimensions of each

specimen. Data were tabulated as the average value of all specimens tested under the same conditions of stability in each study.

Atterberg limits

Atterberg limits were determined by A.S.T.M. Designation: D 423-54T and D 424-54T (1). Since the samples to be tested were stabilized cylinders of material, it was necessary to crush the samples with a mortar and pestle until 100 per cent passed a No. 40 sieve. Mixing and kneading was difficult but was continued until the mass was homogeneous.

Freezing and thawing studies

Samples to be tested in freeze-thaw studies were mixed and molded in the manner outlined previously. After curing for 10 days all samples were weighed, measured for height, and immersed in distilled water for two hours. This was done before the first freeze thaw cycle only. The samples were then placed on water saturated felt pads in pans and frozen at -10 degrees Fahrenheit for 23 hours. The pans, containing the samples, were then removed and distilled water added until the liquid level was just below the top of the felt pads. The samples were allowed to thaw, exposed, at room temperature for two hours. The pan was then covered with Saran wrapping and kept at room temperature for another

23 hours. The foregoing treatment was considered to be one cycle and three samples were tested after each cycle. The samples to be tested were removed, weighed, measured for height change, and immediately tested for unconfined compression.

Three samples from each batch were allowed to air-dry for 30 days after nine cycles and then subjected to a final cycle of freezing and thawing. The specimens were then tested in the same manner described above.

Wetting and drying studies

Specimens to be tested in this study were prepared as previously outlined. After the required curing period all samples were weighed, measured for height, and immersed in distilled water for 24 hours. The samples were removed and all but those to be tested were allowed to air-dry for 24 hours. A complete cycle of wetting and drying consisted of 24 hours air drying followed by 24 hours immersion.

The samples to be examined were blotted dry with paper towels and measured for height change. They were then placed in open, individual moisture cans and weighed. After weighing the samples were tested for unconfined compression, while resting in the open cans. Any flakes or chips broken from the sample were confined inside the moisture can. The moisture can and the entire sample were placed in an oven,

maintained at 100-110 degrees Centigrade, for 24 hours, cooled for one hour in a dessicator, and weighed. This procedure provides an accurate moisture determination and makes possible an accurate determination of any physical loss of the sample due to the wetting and drying treatment.

Differential thermal analysis

Differential thermal analysis is a technique generally used to aid in the identification of clays, minerals, and other crystalline chemicals. The unknown sample is heated simultaneously with an inert material such as calcined alumina. Both sample and inert material are heated at a constant rate and their temperature difference is recorded on a strip chart by means of a differential thermocouple. The temperature of the block is recorded on a separate strip chart.

Each mineral or chemical undergoes characteristic reactions that occur at specific temperatures. These reactions are either endothermal or exothermal in nature and are revealed together with the temperature at which they occur when the two strip charts are correlated. The theory of differential thermal analysis is further discussed by Kerr et al (21).

Differential thermal curves were obtained from a number of aniline-furfural stabilized specimens. The samples varied

in magnitude of clay content as well as in the amount of aniline-furfural contained. The samples used were material salvaged from unconfined compression tests. The coarse pieces were gently ground to pass a No. 40 sieve before the sample was placed in the differential thermal apparatus. Curves were also obtained from a sample of each soil without any aniline-furfural present.

Microscopic and photographic examination

Samples of all soils stabilized with aniline-furfural were visually examined under a binocular microscope. Both catalyzed and non-catalyzed pure aniline-furfural resins were also examined.

Color photomicrographs were taken of the pure resins as well as of resin stabilized soils.

PRESENTATION AND DISCUSSION OF RESULTS

Standard methods for the evaluation of the effectiveness of soil stabilizing chemicals have not been established and correlated with field performance. Since such criteria are lacking it is not possible to make any specific predictions concerning field use of aniline-furfural stabilized soils. Laboratory investigations, however, do produce mixture designs that appear to give the most efficient performance for any one soil.

Theoretical considerations of causes and effects in chemical soil stabilization have, in the past, been kept in the background in favor of the more direct approach of empiricism. This study has been conducted primarily on the premise that a fundamental knowledge of soil stabilization phenomena provides the best approach to the most satisfactory end.

Exploratory Studies

Initial exploratory experiments were run using soils 20-2 and 44A-1 in which the amount of water added was varied together with the percentage aniline-furfural. The ratio of aniline to furfural was 2:1 on a volume basis. The results

from these tests were quite erratic but clearly indicated that maximum stability occurs in the neighborhood of maximum density. It was also apparent that aniline and furfural are not liquids that replace equivalent volumes of water for density requirements. Wet and dry strengths showed a marked increase with water content as optimum moisture was approached. However, the treatment with aniline-furfural exhibited water-proofing ability even when it was mixed with the soil without the beneficial effects of water.

Since it was evident that a large volume of water, compared to the volume of chemicals, was necessary for good stabilization it was decided to observe the behavior of aniline and furfural under water. Aniline and furfural in a molar ratio of 2 mols of aniline to 1 mol of furfural were carefully measured into an Erlenmeyer flask and covered with distilled water. The contents of the flask were vigorously shaken and the flask set aside to allow the reaction to proceed. The water was somewhat discolored and the chemicals formed a layer on the bottom of the flask. After a few days the chemical layer was very dark but still remained a liquid. The reaction progressed with time as evidenced by a notable decrease in viscosity of the chemical layer. The mass did not become solid until nearly a month had passed at which time the resin formed had taken on a very dark color.

Aniline and furfural mixed in the 2:1 mol ratio, in an

open beaker, without any catalyst, begin to react immediately on contact. A red color appears, heat is evolved, and the liquids become cloudy. The chemicals set up into a tarry mass within a few days but the reaction proceeds very slowly thereafter. One such mass of reacted aniline and furfural was poured onto a paper and allowed to spread. The resin tended to get harder and more brittle where it was the thinnest.

Hydrochloric acid is an excellent catalyst for the promotion of the resin forming reaction of aniline and furfural. The resin produced when hydrochloric acid is used is very brittle and dark purple in color. A small amount of the acid added to a stoichiometric mixture of aniline and furfural produces spectacular results. The chemicals begin fuming immediately and once the reaction has started it progresses rapidly with such an evolution of heat that the mixture commences to boil. The boiling becomes violent and then abruptly ceases with the completion of the resin formation.

The employment of hydrochloric acid as a catalyst for aniline-furfural resinification in the calcareous Iowa loess is out of the question because of the carbonate content. Any acid introduced into the soil is immediately consumed in the decomposition of the calcareous material present. The use of a large amount of acid would completely destroy the carbonates and leave free acid for use as a catalyst but this

would involve considerable quantities of acid. This would be impracticable as well as prohibitively expensive.

Figure 3 shows two color photomicrographs of aniline-furfural resin. The resin that has been reacted under water shows a decided tendency toward a brown color while the acid catalyzed resin is purple.

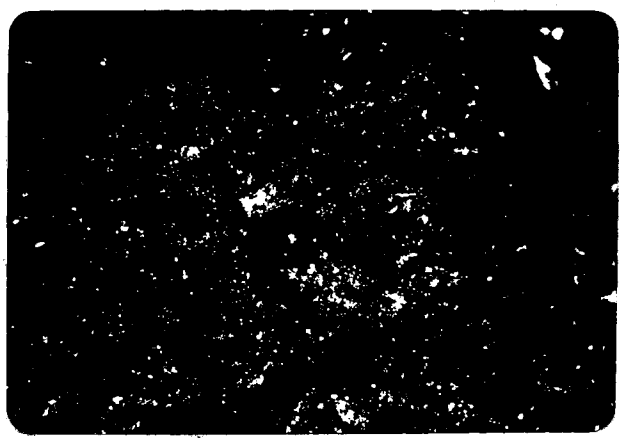
Moisture Determination in the Presence of Aniline-Furfural

Moisture determinations were made both by calculating the amount of moisture from the known initial conditions and by use of an equation developed by the author from experimental results. The two methods were in good agreement and were never more than one-quarter of one per cent in difference. The first method has been used because of its simplicity.

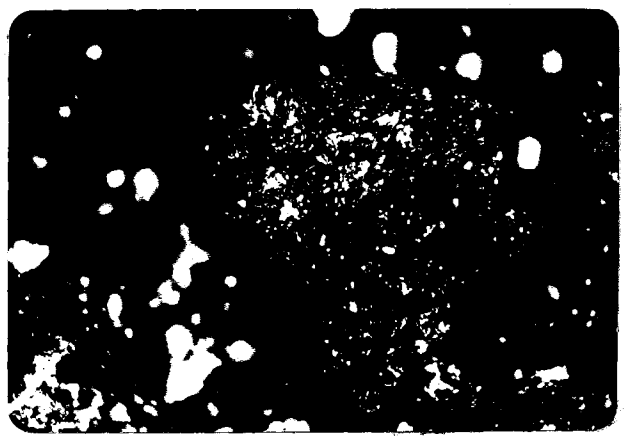
The equation for moisture content was developed from an empirical equation describing the loss of aniline-furfural from small batches that were oven-dried and from simple material balances.[1] The empirical equation and the final moisture equation are as follows:

Empirical equation $P = R + 17$

[1] Material in minus material out equals material accumulated.



Hydrochloric acid catalyzed (x 22.5)



Reaction carried out under water (x 22.5)

Figure 3. Color photomicrographs of aniline-furfural resin

where P = per cent of original chemicals lost

R = ratio of moisture to the amount of aniline-furfural introduced.

Equation developed $M = 99\ L - 0.168\ p\ (1 - L)$

where M = true moisture content

L = ratio of volatile materials lost in oven-drying to the residual material after oven-drying

p = amount of chemicals introduced originally in per cent.

The method which Ogilvie (29) has used for moisture determination presents an interesting feature upon mathematical examination.

Let W = weight of water in the sample in grams

S = weight of soil in the sample in grams

A = weight of aniline-furfural in grams

L = loss of aniline-furfural on oven drying in grams

P = per cent of water in the sample.

Using the above symbols the correct percentage of water is given by the following equation:

$$P = \frac{W}{S} \times 100$$

According to Ogilvie (29) the moisture content may be expressed as the ratio of the total volatiles lost to the residue remaining after oven drying. Expressed as an equation, using the above symbols, the moisture content is given

by:

$$P = \frac{W + L}{S - (A - L)} \times 100$$

Since the two percentages are identical they may be equated and the loss may be found.

$$\frac{W}{S} \times 100 = \frac{W + L}{S + (A-L)} \times 100.$$

Clearing the fractions

$$WS + WA - WL = WS + SL.$$

Combining like terms and solving for the loss the following equation is obtained:

$$L = \frac{W}{S + W} \times A.$$

The ratio of the water to the soil plus water is seen to be the fraction of the aniline furfural lost. Since the optimum moisture content for most of the soils is in the neighborhood of 20 per cent of the weight of soil the loss of aniline-furfural on oven drying is approximately one-sixth of the original amount.

$$L = \frac{20}{100 + 20} \times A = \frac{1}{6} \times A.$$

Actually the loss of aniline-furfural varies from a minimum of one-ninth of the 11 per cent introduced in soil No. 36-1 to one-fifth of the 2 per cent introduced in soil No. 503-2. This bears out the fact that the amount of aniline-furfural lost is dependent upon the amount of water initially mixed into the soil.

A similar derivation using the equation for moisture

content derived by the author produces comparable results. However the resulting equation is rather bulky and lacks the simplicity of the above derivation.

No doubt, some such relationship exists between the loss of aniline-furfural, during air-curing, and the amount of aniline-furfural originally introduced. However, no convenient method for the determination of this relationship exists. The magnitude of the loss during air-curing is probably much less since the vapor pressures of water, aniline, and furfural are all considerably less at room temperatures than they are at oven temperatures.

Density Variations Within 2 x 2 Specimens

A comparison of densities within samples of soil 20-2 stabilized with 11 per cent aniline-furfural is shown in Table 6. The same compactive effort was applied, in both cases, by dropping a 5 pound hammer a distance of one foot a total of 10 times. The specimens that were compacted with an equal number of blows exhibit a more uniform and symmetric density. The compactive effort is also more efficient when applied to both ends as evidenced by a higher average density.

Table 6. Comparison of densities within specimens of soil 20-2 stabilized with 11 per cent aniline-furfural and subjected to different compactive methods

Position in sample	10 blows on one end only		5 blows on each end	
	Density		Density	
	g per cc	lb per cu ft	g per cc	lb per cu ft
Top quarter	1.721	107.4	1.726	107.8
Mid-top quarter	1.676	104.6	1.691	105.7
Mid-bottom quarter	1.676	104.6	1.680	104.9
Bottom quarter	1.693	105.8	1.715	107.1
Average	1.691	105.6	1.703	106.4

Compactive Effort Study

The Harvard miniature compactor was used as a criterion for determining the number of hammer drops to be used in molding 2 x 2 specimens of aniline-furfural stabilized soil. The densities obtained by use of the Harvard apparatus were compared to those obtained from different compactive efforts with the 5 pound hammer.

A plot of optimum dry density obtained for soil No. 20-2 versus the total number of blows delivered in compaction by the drop hammer was made. The number of blows required for each percentage of aniline-furfural was determined by finding the point on the curve that corresponds to the optimum dry

density obtained with the Harvard compactor. The values obtained in this manner were then plotted as the total number of blows used versus the per cent aniline-furfural employed.

Table 7 shows a comparison of the densities and optimum moisture requirements obtained by the two methods. Figure 4a shows a plot of the results while Figure 4b is a plot of data obtained from Figure 4a. Fibure 4b indicates that six blows on each end should be used for compaction without aniline-furfural, seven blows on each end for an aniline-furfural content of from 1 to 3 per cent, and eight blows on each end for the range of 4 to 11 per cent.

Soil 44A-1 did not produce a satisfactory moisture-density curve as shown in Figure 5. However, the optimum moisture was revealed by a plot of dry-strength versus the moisture content at molding as shown in Figure 6. It was therefore concluded that both moisture-density and moisture-strength curves should be used in determining the optimum moisture content.

The voids are nearly filled by the aniline-furfural added as shown by the curve in Figure 7. The curve is approximately a straight line passing through the origin with a slope of 0.77. A line passing through the origin with a slope of one would indicate 100 per cent of the resin was used in filling voids. About three-fourths of the resin appears to be used in filling voids.

Table 7. Comparison of densities and optimum moisture requirements for the Harvard miniature compactor and the 2x2 compaction apparatus using different compactive efforts

Aniline-furfural content %	Harvard compactor		5 blows on each end		7 blows on each end		9 blows on each end	
	Stable density lbs/ft^3	Dry density lbs/ft^3	Stable density lbs/ft^3	Dry density lbs/ft^3	Stable density lbs/ft^3	Dry density lbs/ft^3	Stable density lbs/ft^3	Dry density lbs/ft^3
0		104.4		103.3		105.2		106.0
Opt. M.C.		18.5%		18.5%		18.5%		18.5%
5	105.4	101.0	103.5	99.7	104.8	100.5	*101.2	*98.0
Opt. M.C.	16.5%	17.0%	17.0%	17.3%	16.8%	17.0%	18.5%	18.0%
11	108.5	99.0	106.3	97.3	108.0	98.4	108.6	99.2
Opt. M.C.	13.0%	13.0%	13.0%	13.0%	12.5%	12.2%	11.3%	11.8%

*3 blows on each end

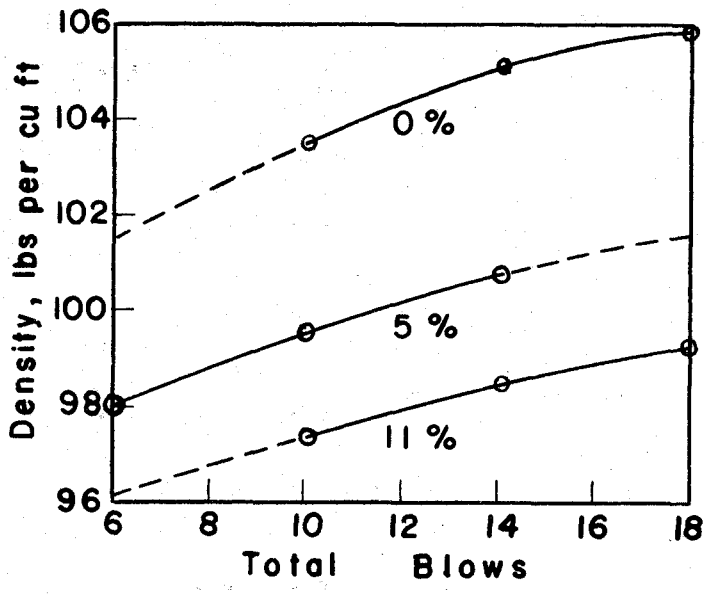


Figure 4a. Density as a function of total number of blows using soil 20-2 and various percentages of aniline-furfural

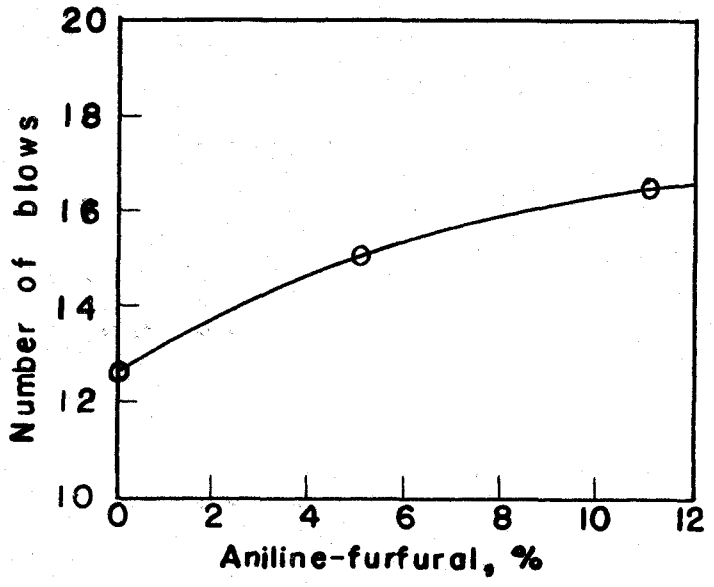


Figure 4b. The number of blows required to give standard Proctor density as a function of aniline-furfural content. Taken from Figure 4a

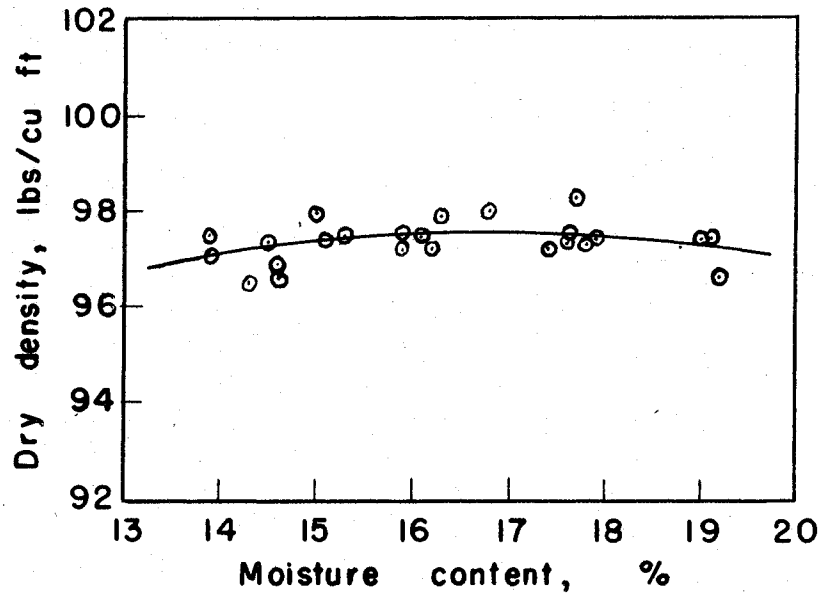


Figure 5. Moisture-density curve for soil 44A-1 mixed with 5 per cent aniline-furfural

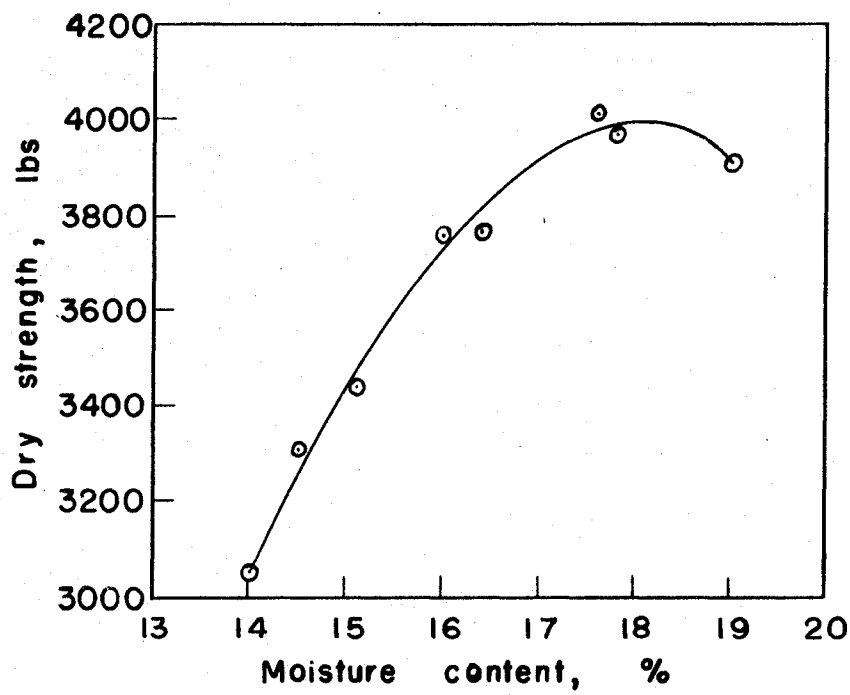


Figure 6. Moisture-strength curve for soil 44A-1 stabilized with 5 per cent aniline-furfural

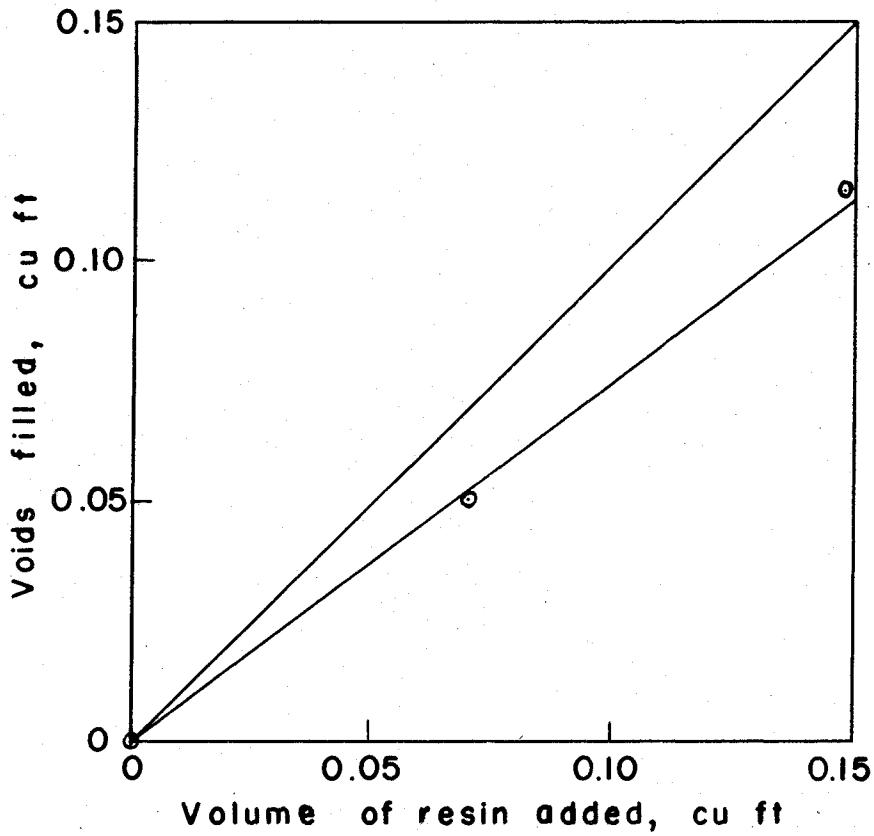


Figure 7 . The volume of voids filled after stabilization as a function of the volume of aniline-furfural added in soil 20-2. The 45 degree line represents the theoretical function if the volume resin added filled an equal volume of voids

Aniline-Furfural Ratio

The data in Table 8 clearly indicate that a weight ratio of 2 aniline to 1 furfural is an optimum ratio. Plots of the data show that the maxima occur slightly below the 2:1 ratio. A weight ratio of 1.931:1 is a 2:1 mol ratio which is an exact

Table 8. Aniline-furfural ratio study data

Weight ratio of aniline to furfural	Dry strength lbs	Wet strength lbs	Weight loss during curing %	Moisture absorption after 24 hrs immersion %
1:4	1530	190	17.3	15.3
1:2	1630	390	16.6	14.2
2:2	1310	400	15.5	16.1
3:2	2430	1090	15.2	2.9
4:2	2790	1240	15.4	2.2
5:2	2540	1070	15.3	2.6
6:2	2100	580	15.7	10.7

stoichiometric relation between aniline and furfural as proposed by Zincke and Muhlhausen (45) and supported by Winterkorn (43). Ratios as low as 3:2 and as high as 5:2 could be used without drastic departure from optimum conditions.

Order of Mixing

The results of the study previously described indicate that the mixing order of water, furfural, and then aniline produces the best all around product. The second best mixing order was found to be furfural, water, and aniline. Mixing furfural in last produces fair results while mixing water in last was definitely shown to be poor procedure.

The results are but slightly better when water is mixed in first than they are when furfural is mixed first. In any case it is important that the aniline be mixed in last. This is probably due to the relative solubilities of aniline and furfural in water and to the preferential absorption of furfural by the clay minerals. A table of gel volumes quoted by Grim (16, p. 267) presents values of organic absorption by bentonite as determined by Jordan (19).

All mixtures used in this study were henceforth made by mixing the water and furfural simultaneously until the mass was homogeneous. Aniline was mixed in last, just prior to molding.

Drying Study

A typical drying curve is presented in Figure 8. The drying curves for 0, 1, 3, 7, 9, and 11 per cent aniline furfural are very similar in nature and vary mainly in initial

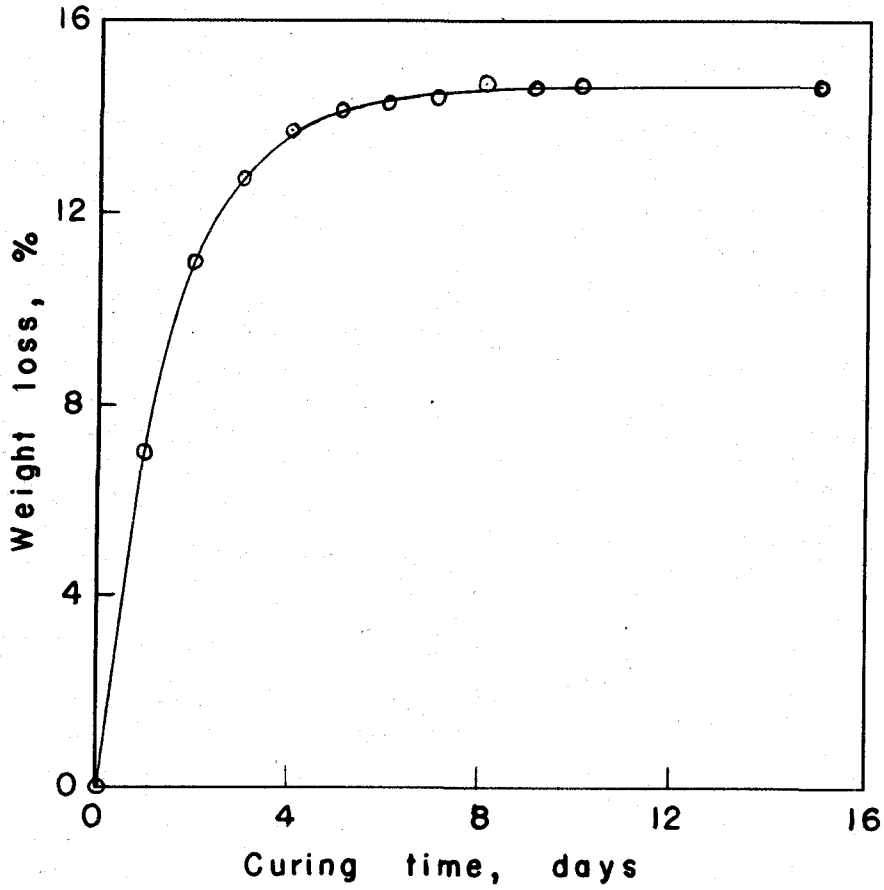


Figure 8. The total weight per cent of volatile material lost in curing plotted against the time of curing in days for soil 20-2 using 5 per cent aniline-furfural. Similar curves were obtained for other percentages of resin

slope and in magnitude of the final constant loss. The minimum radius of curvature for each curve tends to increase with an increase in aniline-furfural content. The samples were nearly dried after five days of air-curing and had reached equilibrium after eight days in all cases. The loss percentages were calculated on the basis of the stable weight of the samples.

Final losses after 15 days air-curing and the total losses on oven-curing are plotted for each percentage aniline-furfural in Figure 9. The small rise in the volatile loss curve after 15 days air-curing is evidently due to the loss of some of the stabilizing chemicals. The difference between the air-dry curve and the oven-dry curve in Figure 9 is the hygroscopic moisture retained. A plot of this data is made in Figure 10a and shows a rapid decrease in hygroscopic moisture with increased chemical treatment until 7 per cent is reached. The hygroscopic moisture then remains constant for 7, 8, and 11 per cent.

The total losses after 15 days air-curing were recomputed as a percentage of the total volatile material in the samples initially. These values were then plotted versus the per cent aniline-furfural employed as shown in Figure 10b. There appears to be a maximum loss of volatile material near 5.5 per cent chemical treatment. This phenomenon may possibly be explained by the amounts of materials present.

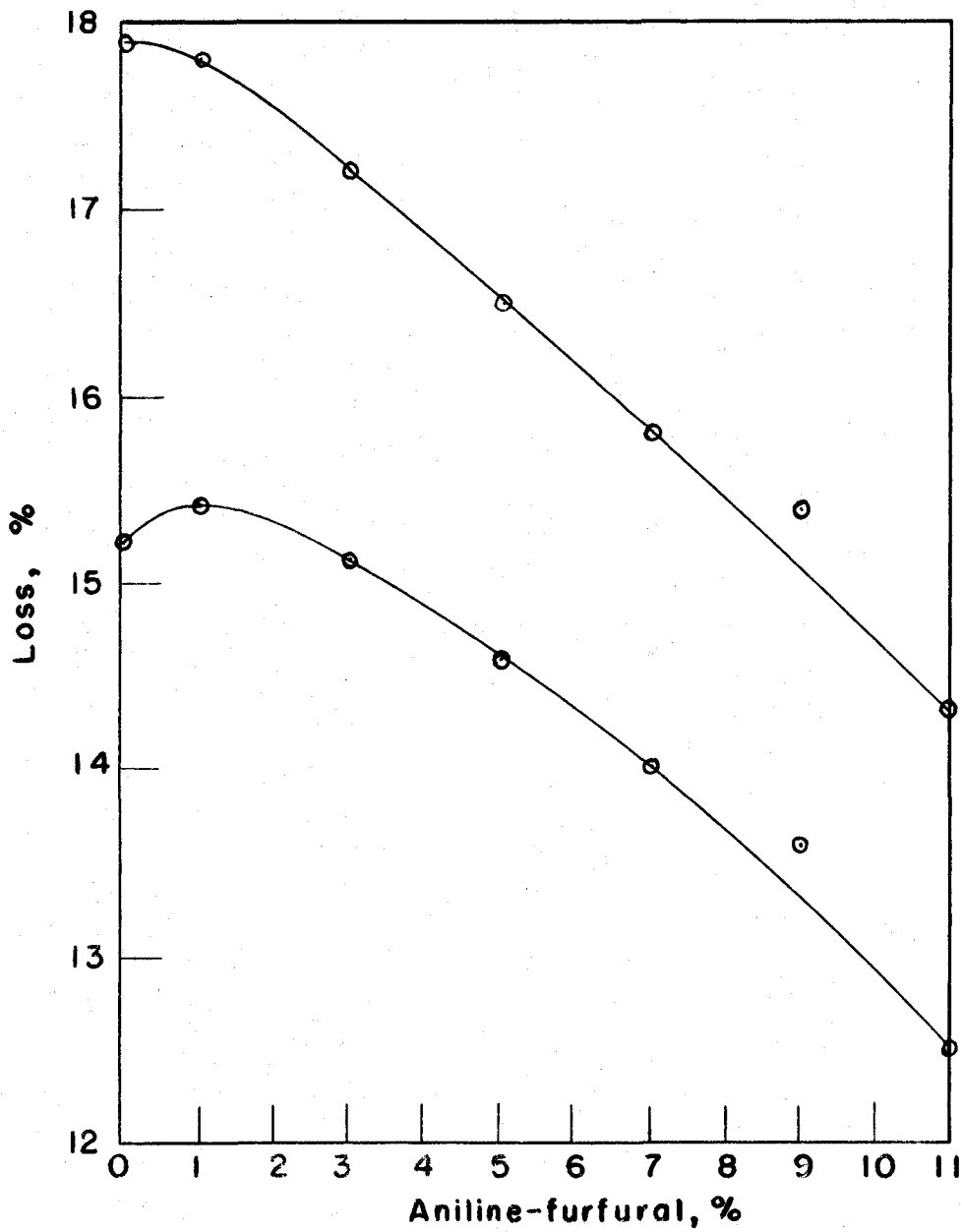


Figure 9. The weight loss on curing as a function of aniline-furfural content is plotted in the lower curve for soil 20-2. The upper curve is the weight loss after oven-drying

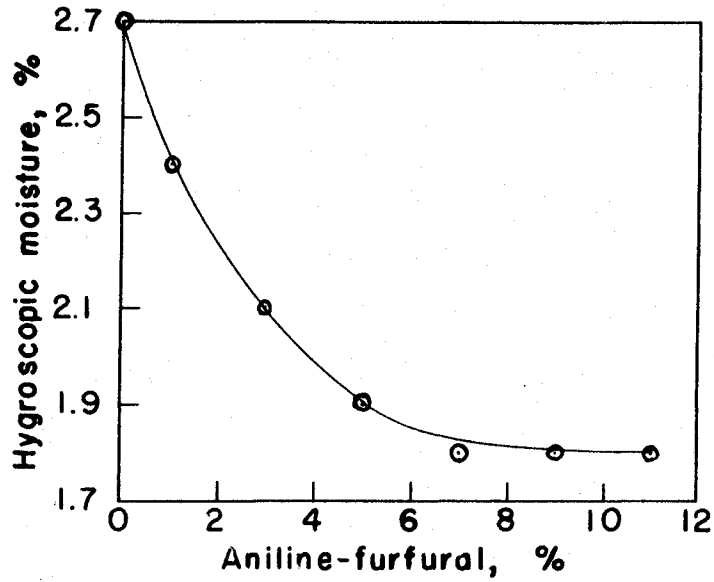


Figure 10a. Hygroscopic moisture plotted against aniline-furfural content for soil 20-2

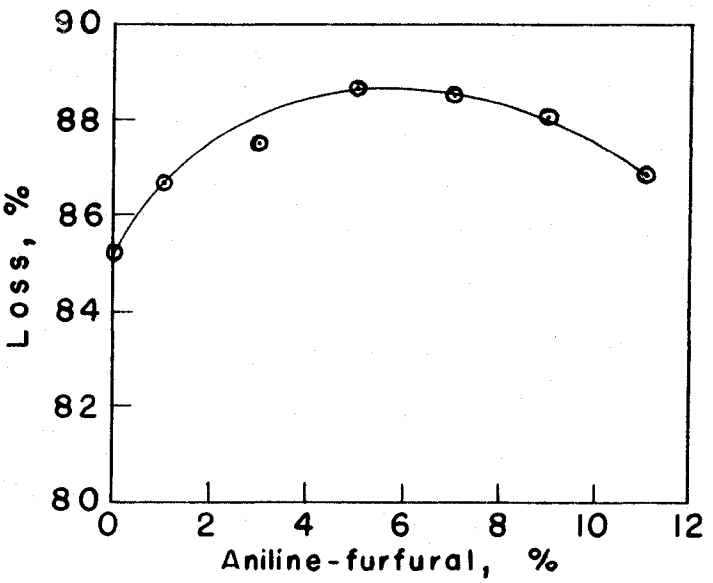


Figure 10b. The volatile loss as a per cent of the total volatile material plotted against the aniline-furfural content for soil 20-2

Since a completely homogeneous mixture is almost surely an impossibility, the reacting chemicals will not be found in a 2:1 ratio in all parts of the mix. Above a 5.5 per cent treatment the chemicals are probably in contact enough to react rapidly so as to trap any unreacted material long enough to react completely. Another possibility is presented by the thermodynamic situation. If the quantities of chemicals present are such that their heat of reaction is great enough to overcome heat losses the temperature rise of the overall mass should further promote the reaction rate. A rapid reaction rate would decrease volatile losses by precipitation of the nonvolatile resin.

The samples used in the drying study were further tested for air-dry strength, strength after 24 hours immersion in distilled water, and for deformation at failure, both wet and dry. The deformation curves are plotted in Figure 11. They show an interesting relationship to Figure 10b in that the maximum volatile loss and the minimum deformation occur at the same or nearly the same percentage of chemical treatment. Evidently the quality of resin is much better at this percentage than at any other percentage since a hard resin does not deform as much as a softer resin when tested to failure. It was also noted that a tendency for the specimens to fail suddenly rather than gradually occurred in this range of chemical treatment.

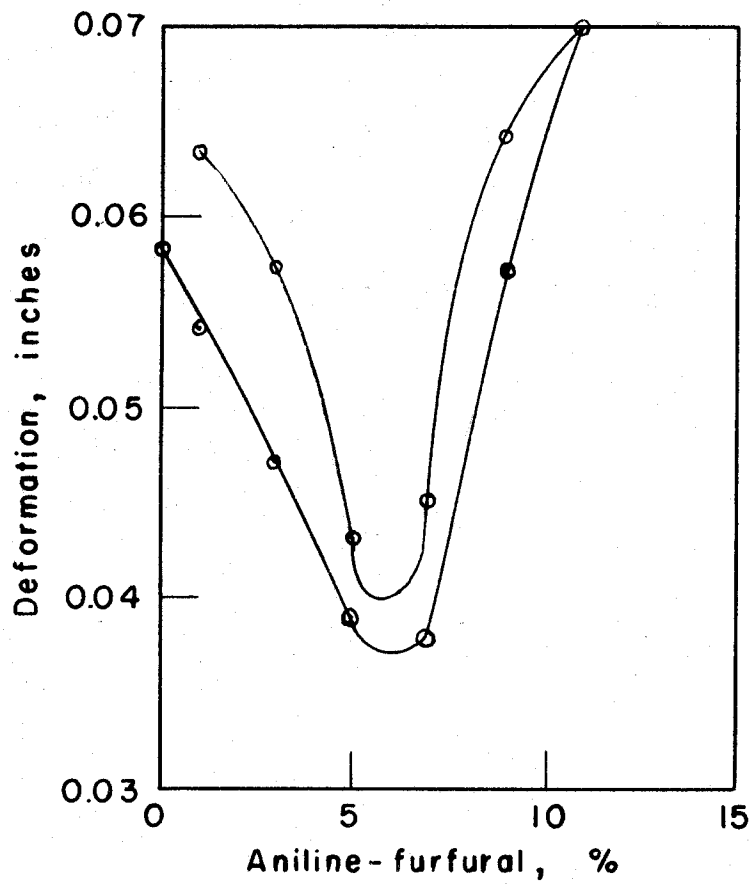


Figure 11. The deformation at failure in unconfined compression testing as a function of aniline-furfural content in soil 20-2. The upper curve is for wet testing and the lower curve is for dry testing

Figure 12 presents the strength data for air-dry strength, oven-dry strength, and for strength after immersion. Both the air-dry and the oven-dry curves exhibit a loss in strength with a low chemical treatment. The air-dry strength regains that of compacted soil alone at about 4 per cent chemical treatment while the oven-dry specimens require about 8 per cent treatment. The oven-dry specimens are probably inferior because of shrinkage stresses induced by the loss of moisture in the clay particles. The initial loss of air-dry strength is thought to be due to partial dstruction of cohesion with consequent loss of some clay cementation. The wet strength increases almost linearly with increased aniline-furfural content. The initial increase is no doubt due to water proofing since the slope does not become constant until about 5 per cent treatment is reached. Any material added in excess of 5 per cent is evidently increasing the strength by mechanical means only and does not aid in waterproofing.

Curing Time

The effect of time on the stability of specimens treated with aniline-furfural is shown by the data in Tables 9 and 10. The strength increases rapidly with time until a maximum is reached in about five to eight days. The strength then drops to a near constant value at about 10 days curing time.

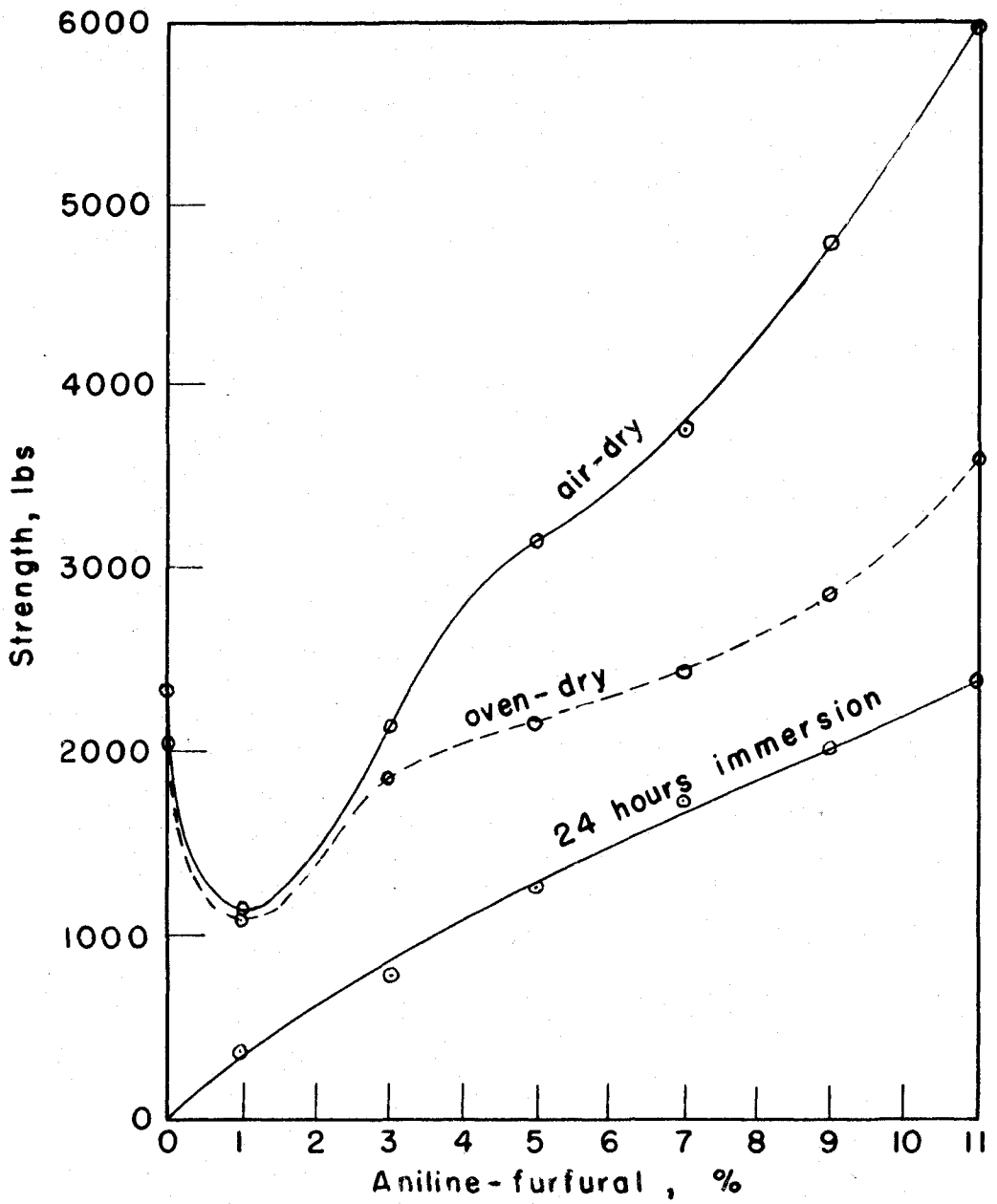


Figure 12. Unconfined compressive strength as a function of aniline-furfural content in soil 20-2. The conditions at the time of testing are shown in connection with each curve

Table 9. Curing time data for soil 20-2 stabilized with 5 per cent aniline-furfural

Curing time	Aniline, furfural and water retained	Moisture absorption after 24 hours immersion	Air-dry strength	Strength after 24 hours immersion
days	%	%	lbs	lbs
0	22.0	-	-	-
1	14.5	failed	380	-
3	7.6	14.4	2070	450
4	7.2	8.2	2525	1000
6	7.0	2.8	3010	1100
7	6.7	3.4	2735	1300
9	6.0	4.2	2925	1070
12	5.7	5.2	2370	1090
17	5.7	3.9	2380	1060
31	5.3	2.2	2380	1540
22 mos.	5.3	1.8	2760	1370

After a 22 months curing period specimens tested dry showed an increase in strength over one month curing. The 5 per cent treatment exhibits an increase in wet strength in one month of curing as well as in 22 months. The 11 per cent treatment also gained in wet strength after 22 months curing.

The absorption of moisture during immersion for 24 hours in distilled water shows a definite tendency to decrease with

Table 10. Curing time data for soil 20-2 stabilized with 11 per cent aniline-furfural

Curing time	Aniline, furfural and water retained	Moisture absorption after 24 hours immersion	Air-dry strength	Strength after 24 hours immersion
days	%	%	lbs	lbs
0	24.0	-	-	-
1	18.8	15.0	560	50
2	16.2	5.1	2155	1310
3	13.9	6.7	4470	1695
4	14.3	4.7	5415	1910
5	12.9	5.6	6515	2100
8	12.2	8.7	6480	2015
13	11.9	8.1	4865	1920
27	11.8	5.4	4680	1890
22 mos.	11.7	1.5	4710	3515

an increased curing period. The resin evidently improves in both strength and the ability to impart hydrophobic qualities to the soil.

A plot of the per cent water plus aniline-furfural retained in the samples versus time produces a curve similar in nature to Figure 8. The range of maximum curvature falls between three and five days. The moisture lost during this period and in the next few days is closely associated with

the clay minerals. The decrease in strength at this time is probably due to shrinkage of the clay away from the network of aniline-furfural resin. If this hypothesis holds true some destruction of the aniline-furfural to clay bond must take place leaving void space for any subsequent re-entry of moisture. However, as indicated by the reduction in moisture absorption with time, any unreacted aniline and furfural must unite and be absorbed by the clay minerals.

Catalysts

Several catalysts were used in an attempt to improve the quality of the resin. Lime, sodium hydroxide, hydrochloric acid, and aluminum chloride were introduced in solutions of volumes equal to the water requirements for optimum density. The hydrochloric acid produced no beneficial results because of its reaction with the carbonates in the soil.

Hydrated lime, in powdered form, was dry mixed with the soil before addition and mixing of water and 5 per cent aniline-furfural. Lime was added in the amounts of 1, 2, 3, 4, and 5 per cent of the oven-dry weight of the soil. The dry strength of the stabilized material varied between 710 and 830 pounds as compared to 2400 pounds with 5 per cent aniline-furfural. The wet strength for all percentages of lime varied between 170 and 240 pounds whereas the wet

strength with aniline-furfural alone was near 1100 pounds. All samples with lime added were moist throughout after 24 hours immersion in distilled water. The dry samples were found to be very powdery and could be crushed in the hand.

Sodium hydroxide shows some promise as an additive and appears to produce a secondary chemical reaction with the soil. The simultaneous addition of sodium hydroxide and aniline-furfural presents a study in itself.

Aluminum chloride was added in solution with the mixing water to the soil and followed by 5 per cent aniline-furfural. The specimens were cured for 10 days and the results are compared to those obtained without the catalyst in Table 11.

The catalyzing effect of the aluminum chloride is immediately apparent during mixing. The mixture takes on a red color as soon as all chemicals make contact. The color is intensified considerably as the amount of catalyst is increased.

Inspection of Table 11 shows that both wet and dry strengths increase when 0.10 and 0.30 per cent catalyst is used. The weight loss after curing and the moisture absorption both decrease with an increase in catalyst. The above behavior indicates a better quality resin is produced by the addition of small amounts of aluminum chloride.

The relationship of the density of the stabilized specimens to the amount of aluminum chloride added is linear with

Table 11. Data obtained using aluminum chloride as a catalyst with 5 per cent aniline-furfural in soil 20-2 II

Aluminum chloride used %	Height loss after curing inches	Height gain after immersion inches	Weight loss after curing %	Moisture absorption after immersion %
0	0.0017	0.0012	14.6	2.2
0.05	0.0021	0.0016	14.2	5.8
0.10	0.0022	0.0015	14.2	5.5
0.30	0.0020	0.0011	14.0	4.5
0.50	0.0019	0.0008	13.5	4.6

	Dry density lb per cu ft	Stable density lb per cu ft	Air-dry strength lbs	Wet strength lbs
0	101.4	104.8	2790	1240
0.05	102.6	107.1	3360	1040
0.10	102.3	106.8	3540	1340
0.30	101.4	105.9	3540	1410
0.50	99.9	104.4	3460	1410

a negative slope. This is thought to be due to the increased reaction rate causing an increase in aggregation before molding can be accomplished.

The data appears to indicate that the best amount of aluminum chloride to add is in the neighborhood of 0.3 per

cent of the oven-dry soil. Mixing becomes difficult, with the addition of 0.5 per cent of this catalyst, due to the increased reaction rate. Addition of larger amounts of catalyst would probably seriously impair mixing and could even prevent it.

An influence of pH on the aniline-furfural reaction was definitely revealed in this study during mixing and after curing. The mixtures made with soils having an acidic pH exhibited a definite red color upon the addition of aniline in the final stages of mixing. By analogy to the hydrochloric acid catalyzed reaction this indicates a definite increase in reaction rate. After curing the color of the specimens shaded from a dark brown to a brown with a purple cast as the soil pH changes from alkaline to acidic. However no quantitative influence of pH could be isolated from the test results.

Moisture-Density Relationships

The moisture-density relationships were established for six soils that represent a wide range in textural variation in the loess. The soils were treated with varying percentages of aniline-furfural and required a different optimum moisture for each per cent studied. A typical group of moisture-density curves for soil 36-1 are presented in Figure 13. The

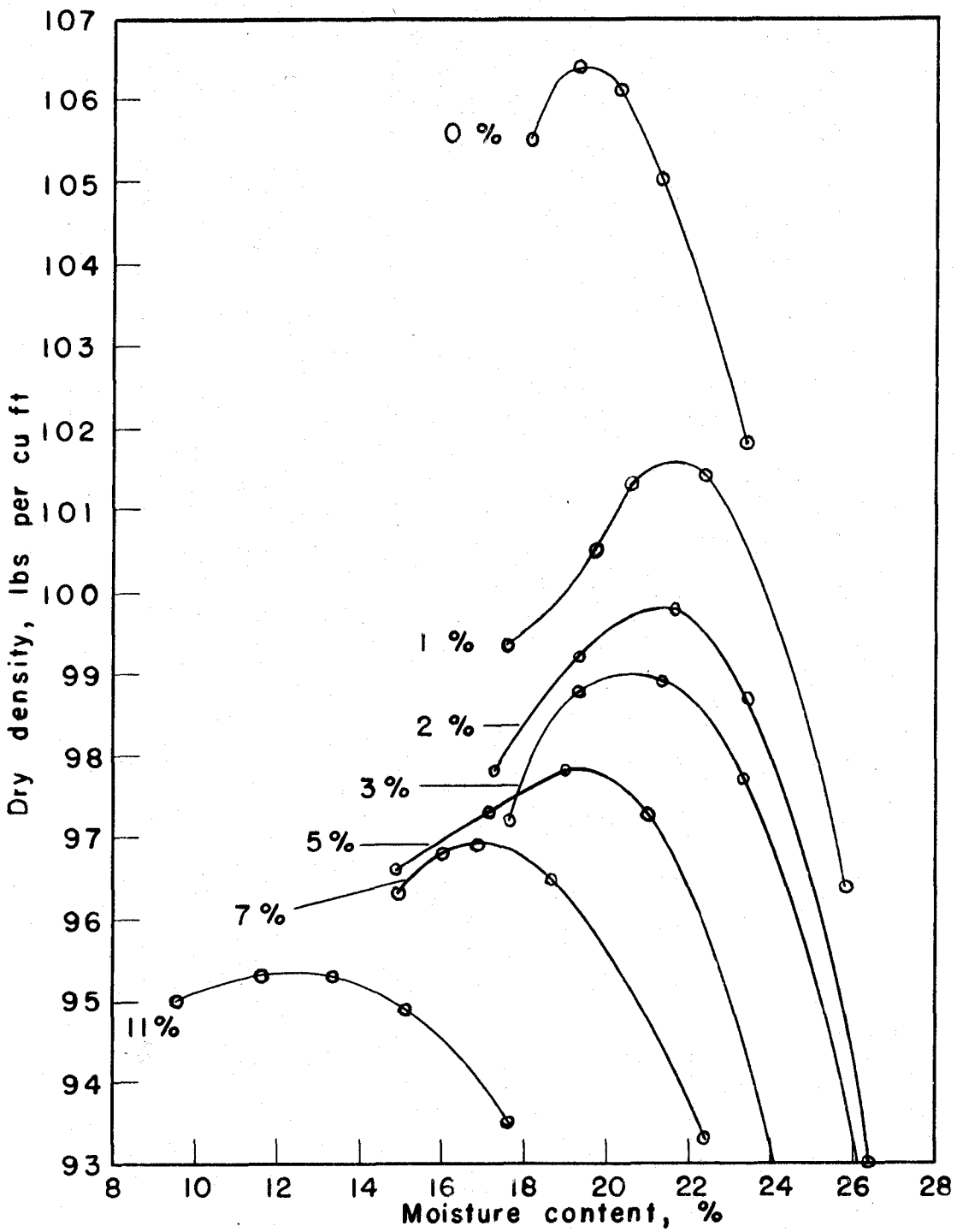


Figure 13. Moisture-density relationship for soil 36-1 stabilized with various percentages of aniline-furfural. The amount of resin treatment is shown for each curve

curves tend to flatten and the densities decrease as the aniline-furfural content is increased.

Figure 14 shows a group of curves in which the optimum moisture is plotted against the aniline-furfural content for the six soils. A close look at these curves reveals that a surface would be formed if the points were plotted in three dimensions. Let the optimum moisture be the dependent variable, the clay content and the aniline-furfural content represent the independent variables. The surface thus visualized would have a saddle point between samples 26-1 and 36-1 which contain 21.7 and 26.3 per cent 2 micron clay respectively. The saddle point also lies between 1 and 3 per cent aniline-furfural content. This indicates a more efficient mixing and use of the liquids as lubricants in densification.

All soils except 55-1 show a maximum amount of optimum moisture requirements between 1 and 2 per cent aniline-furfural. Soil 55-1 has a very low clay content and therefore does not exhibit much aggregation due to the addition of aniline-furfural. This is also apparent during the mixing process.

Strength Results

Aniline-furfural treated loess is quite sensitive to moisture content at molding. This is demonstrated in Figure

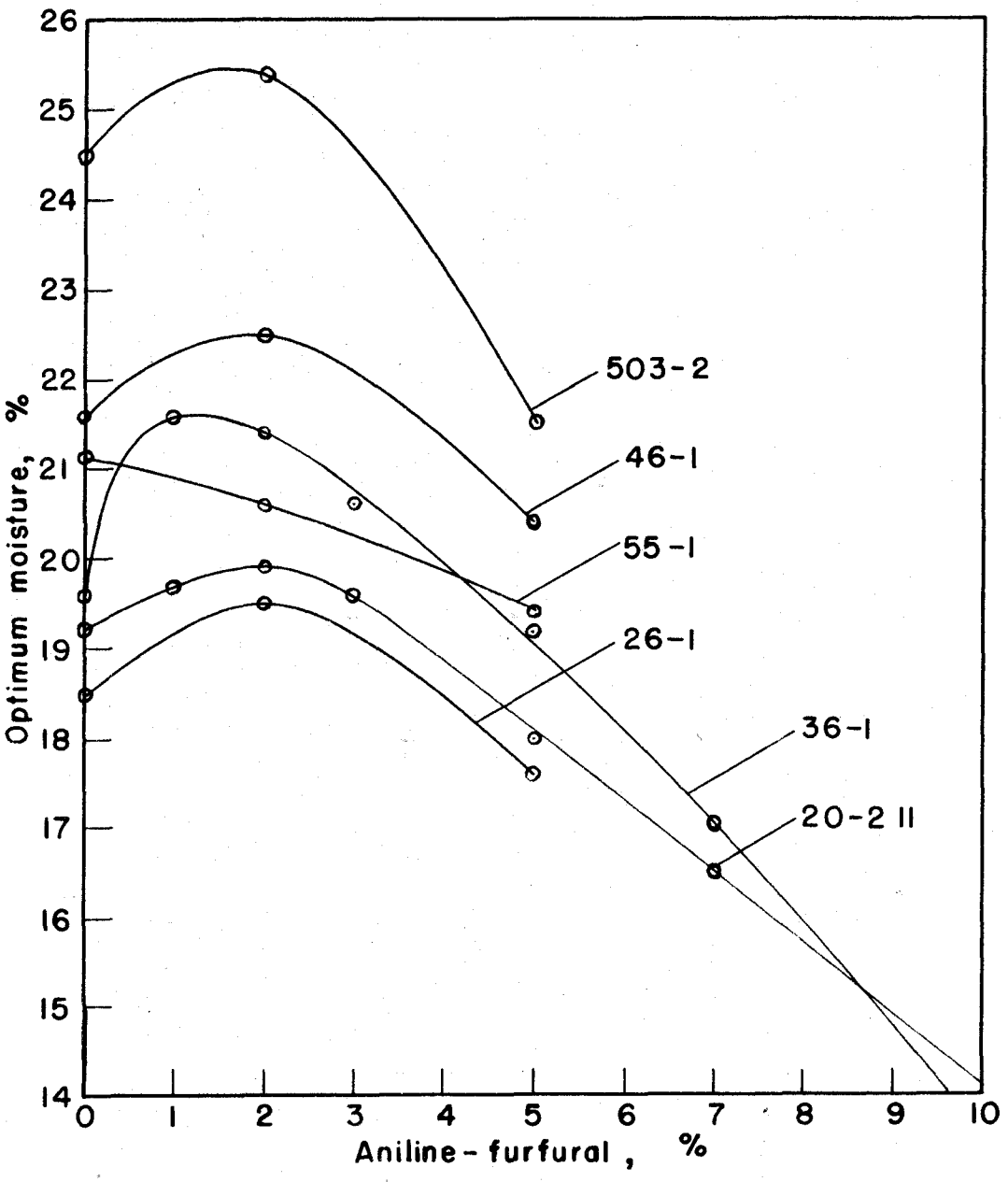


Figure 14. Optimum moisture plotted as a function of the amount of aniline-furfural used in the treatment of six different loess soils. The soil sample numbers are shown with their respective curves

6 where the strength is plotted against moisture content. The optimum moisture content for maximum density was below or equal to that for maximum strength in all cases. However, the two optimum amounts of moisture did not vary more than 2 per cent except in the case of soils 46-1 and 503-2. The wet strengths were still increasing when 3 per cent above optimum moisture for maximum density had been reached. Since the last two mentioned soils are high in clay content, it is thought that the additional moisture aids in the distribution of the aniline and furfural by reducing the size of aggregates. Evidently this aid in dispersion of the chemicals more than offsets the reduction in density caused by too much water.

Soils treated with low percentages of the aniline-furfural resin show a loss in air-dry strength as compared to the untreated specimens. This loss in strength is usually regained before treatment exceeds 5 per cent resin addition. The loss is thought to be due to partial destruction of cohesion between the soil grains because of resin absorption on and in the clay. Apparently at least 2 per cent resin is required for the maximum destruction of cohesion using this method of stabilization.

Figures 15, 16, and 17 show the results of air-dry strength plotted against the aniline-furfural content for the six soils studied. Soil 503-2 failed to exhibit the customary

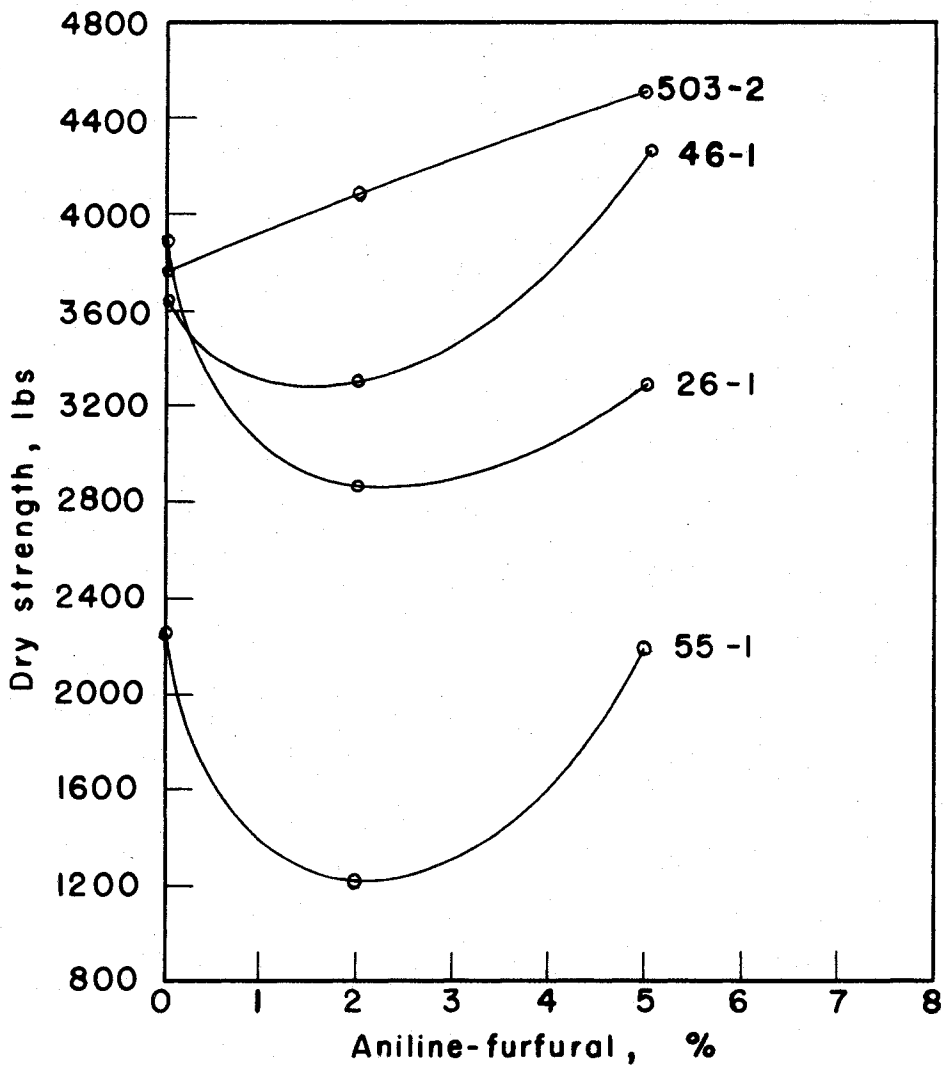


Figure 15. Dry strength as a function of aniline-furfural content for the soils indicated on the graph

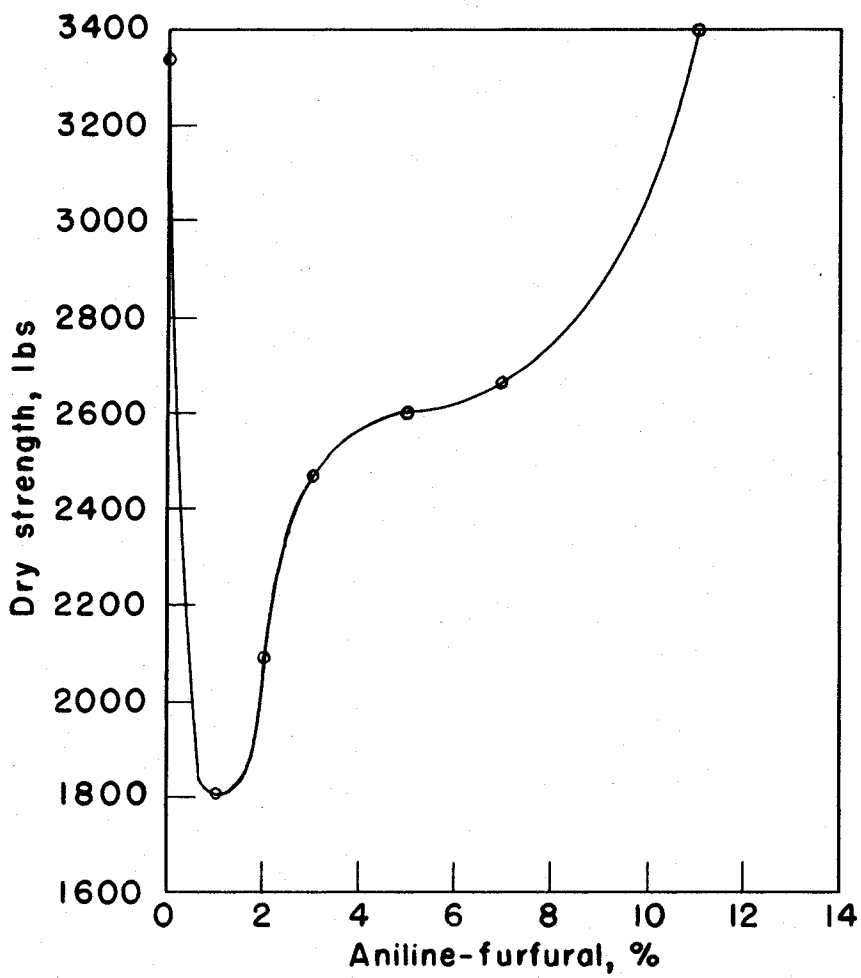


Figure 16. Dry strength as a function of aniline-furfural content for soil 20-2II

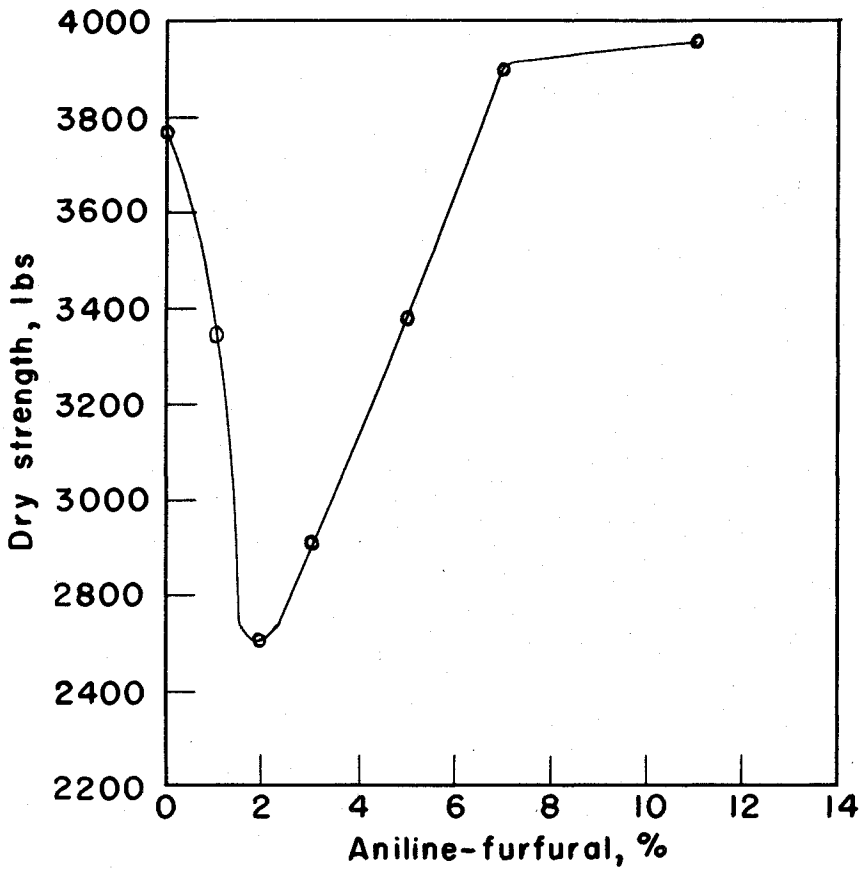


Figure 17. Dry strength as a function of aniline-furfural content for soil 36-1

loss in strength. However the maximum loss, expressed as a per cent of the untreated strength, decreases with an increase in clay content. This indicates that the association of the clay and the aniline-furfural is not entirely complete.

Data obtained from samples that were immersed in distilled water for 24 hours before testing are tabulated in Table 12. Plots of the wet strength versus the 2 micron clay content for 2 and 5 per cent aniline-furfural treatment are shown in Figure 18. A maximum occurs at about 22 per cent clay content in both cases. This is thought to be somewhat due to the degree of aggregation occurring during mixing and compaction.

The soils with the lower clay percentages no doubt are aggregated somewhat on the introduction of aniline-furfural. However they probably do not become aggregated enough to prevent a good association of the clay particles and the resin until 22 per cent 2 micron clay is present. Clay contents above this percentage become aggregated in such large lumps that the chemicals cannot be intimately mixed in with the clay. Visual inspection of mixing bears this out as well as the fact that, when specimens of the higher clay contents are broken, small areas of soil that do not show any of the characteristic resin coloration are visible.

The close association of density and aggregation has been known for a considerable time. Plots of density versus

Table 12. Data obtained from samples after immersion in distilled water for 24 hours

Soil no.	2 micron clay content %	Aniline-furfural content %	Strength after 24 hours immersion lbs	Absorption after 24 hours immersion %	Density lb per cu ft
55-1	7.4	2	490	2.5	97.3
		5	630	9.7	96.3
20-2II	17.8	1	530	5.0	101.3
		2	810	3.4	99.5
		3	980	2.9	99.4
		5	1050	5.2	99.1
		7	1080	11.0	97.6
		11	1260	11.7	96.3
26-1	21.7	2	910	3.7	102.2
		5	1590	2.0	99.9
36-1	26.3	1	550	6.8	101.8
		2	760	5.3	99.9
		3	860	4.8	99.2
		5	890	5.3	97.9
		7	1020	6.2	96.9
		11	1540	7.6	95.4
46-1	26.3	2	670	6.5	97.5
		5	1020	5.3	94.5
503-2	37.0	2	460	8.6	92.4
		5	590	7.8	90.6

the amount of 2 micron clay are shown in Figure 19. Again a maximum is exhibited at a clay content of about 22 per cent indicating a minimum amount of aggregation. However the wet strength maximum cannot be entirely allayed to density since these two quantities show no correlation whatsoever. The

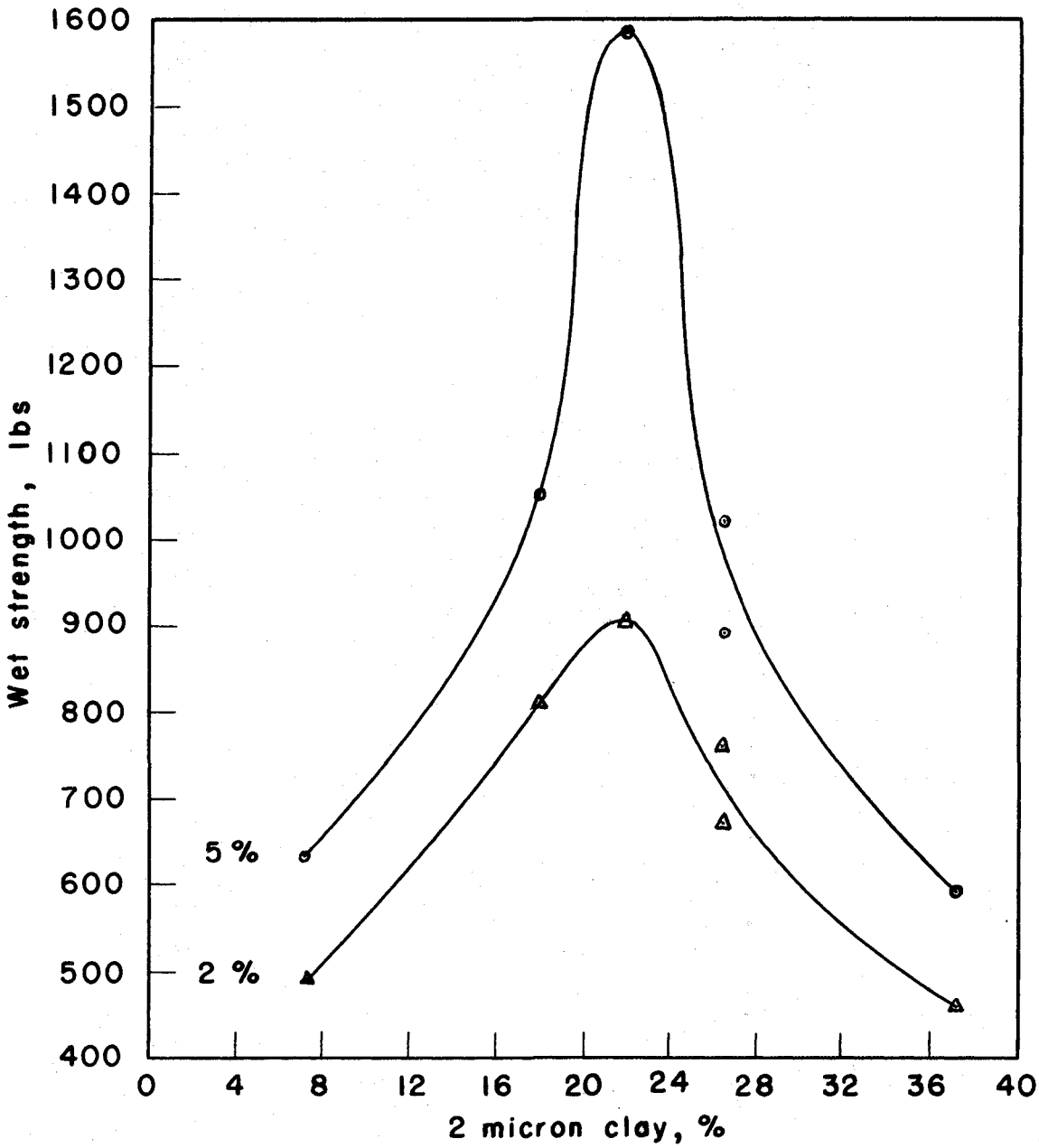


Figure 18. Wet strength as a function of 2 micron clay content of loess stabilized with 2 and 5 per cent aniline-furfural

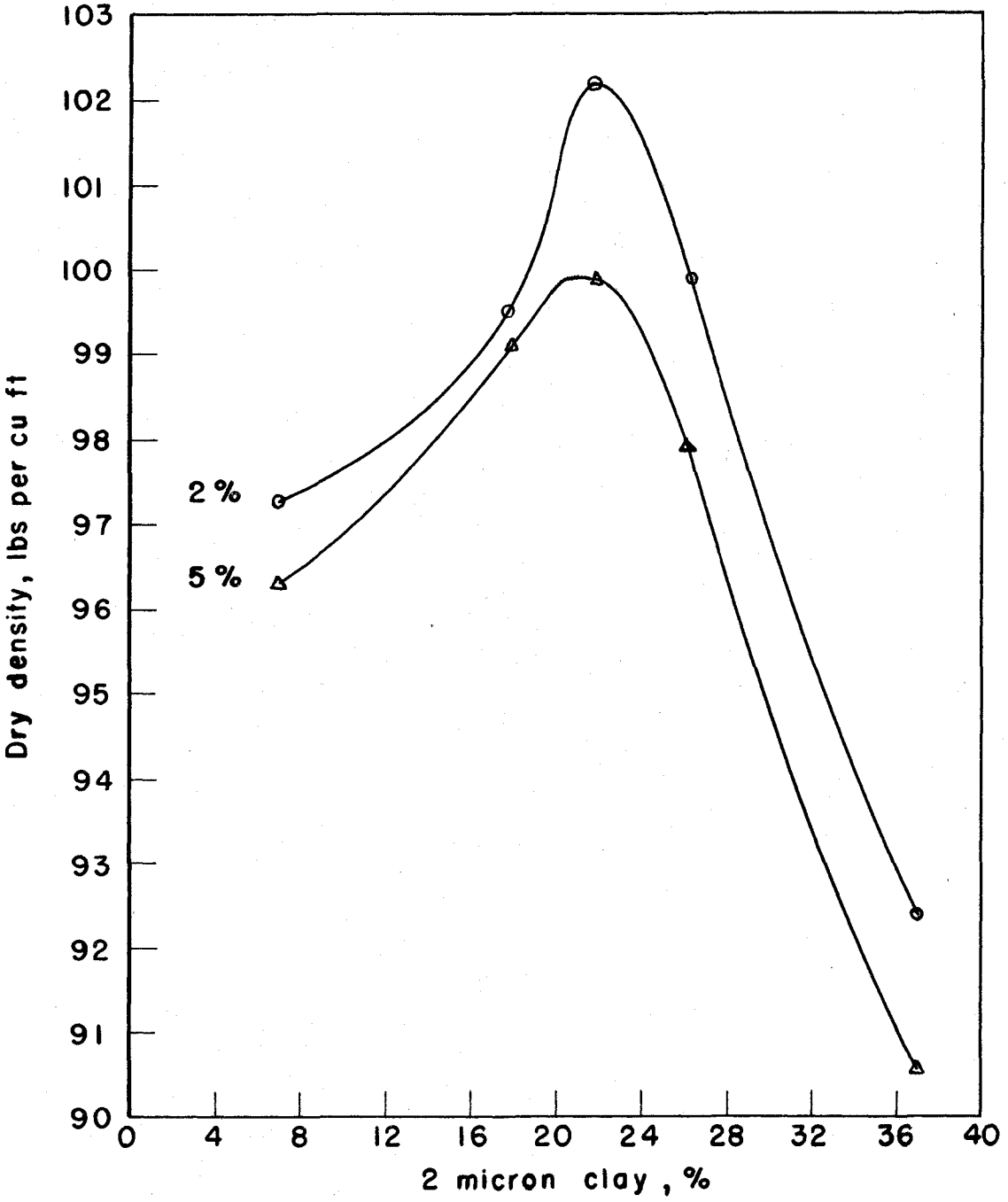


Figure 19. Dry density plotted against 2 micron clay content of loess stabilized with 2 and 5 per cent aniline-furfural

association of the resin with the clay and the density probably both contribute to the high strength since waterproofing prevents weakening on immersion.

Absorption of Moisture

The absorption of water by specimens during immersion in distilled water is shown in Table 12. Both samples 20-2II and 36-1 were treated with a wide range of aniline-furfural and show a maximum waterproofing at 3 per cent resin content. Apparently the clay-resin association is a maximum at this percentage. The increase in moisture absorption with an increase in resin content is more rapid, in the case of the lower clay content soil 20-2II, once the minimum is passed. This also appears to hold true for all the other soils tested.

It appears that a three dimensional plot of the type mentioned before but with the absorption as the dependent variable would yield an absolute minimum. This minimum falls somewhere in the region bounded by 17.8 and 26.3 per cent 2 micron clay and 2 and 5 per cent aniline-furfural according to the data. This supports Winterkorn's findings that the treatment works best with medium plastic soils.

The mechanism of water adsorption by clays is explained in considerable detail by Grim (16) in his book on Clay

Mineralogy. The outstanding feature of the montmorillonite structure is that water and certain organic molecules can enter between the unit layers of the crystal lattice. This causes the lattice to expand in the "c" direction. Exchangeable cations occur between the silicate layers and the c-axis spacing depends somewhat on the size of the interlayer cation. The thickness of the water layers between the silicate units is also dependent on the nature of the exchangeable cations. The foregoing statements are particularly significant since the dominant clay minerals in Iowa loess are montmorillonite types.

Aniline and furfural form into large cations capable of exchanging positions with naturally occurring cations and thus rendering a clay particle hydrophobic. Furfural is also absorbed by clay as shown by Jordan (19) and thus occupies an area from which a large cation may be formed by reaction with aniline. It is even possible that such a cation could enter into the resin formation reaction and still retain its hold to the clay. If such is the case water will be excluded from the clay mineral structure by virtue of space arrangements between the unit cells and by rendering the surfaces hydrophobic.

Differential Thermal Analysis

Differential thermal curves for six different soils treated with various percentages of aniline-furfural are shown in Figures 20, 21, 22, 23, and 24. These thermal curves exhibit characteristic exothermic reactions for soils treated with organic material. Double peaks are between 240 and 800 degrees Centigrade are present for all soils containing 2 per cent or more of aniline-furfural. The double peaks are believed to be caused by initial combusion of readily available resin followed by a final burning of the remaining aniline-furfural. The final combustion does not take place until the breakdown of the clay crystal structure occurs at about 550 degrees Centigrade. A close association of the resin and the clay minerals is indicated by this phenomenon. Strong evidence of this association is found in the correlation of the amount of clay present and the temperature difference between the two peaks. The amount of resin must be the same in each soil used for the thermal curves in this correlation. Plots of the clay content against the temperature difference between peaks are shown in Figure 25. The peaks are marked on the thermal curves shown in the figures.

An excellent discussion and analytic proof of quantitative relations between the area under a peak and the amount

Figure 20. Differential thermal curves for loess samples 46-1 and 55-1 stabilized with various percentages of aniline-furfural as indicated on the left hand side of the curves. The top three curves are for sample 46-1 and the bottom three are for sample 55-1

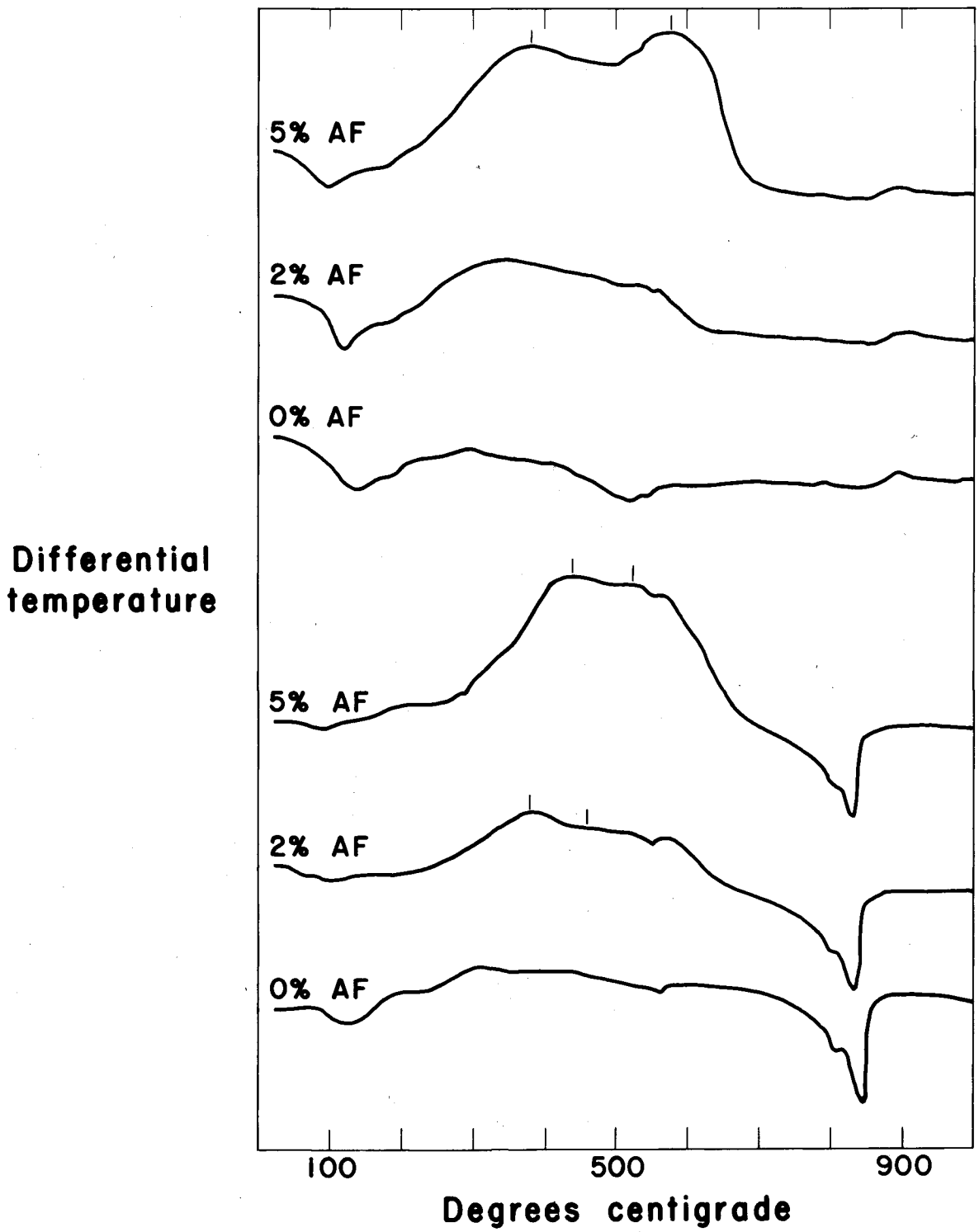

5% AF
2% AF
0% AF
5% AF
2% AF
0% AF
Differential temperature
100
500
900
Degrees centigrade

Figure 21. Differential thermal curves for loess samples 26-1 and 503-2 stabilized with various percentages of aniline-furfural as indicated on the left hand side of the curves. The top three curves are for sample 503-2 and the bottom three are for sample 26-1

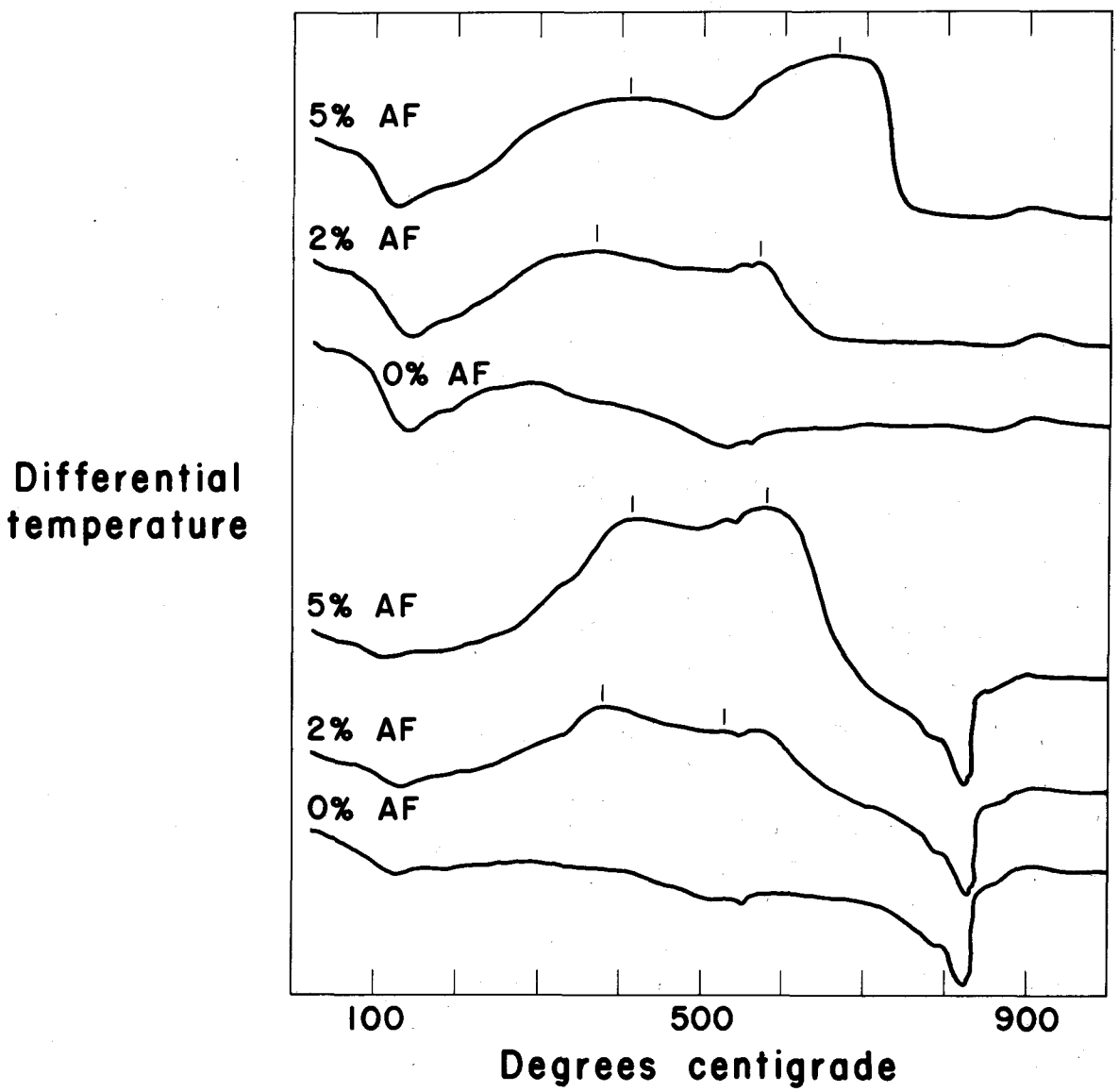

5% AF
2% AF
0% AF
5% AF
2% AF
0% AF
Differential temperature
100
500
900
Degrees centigrade

Figure 22. Differential thermal curves for loess sample 20-2II stabilized with various percentages of aniline-furfural as indicated on the left hand side of the curves

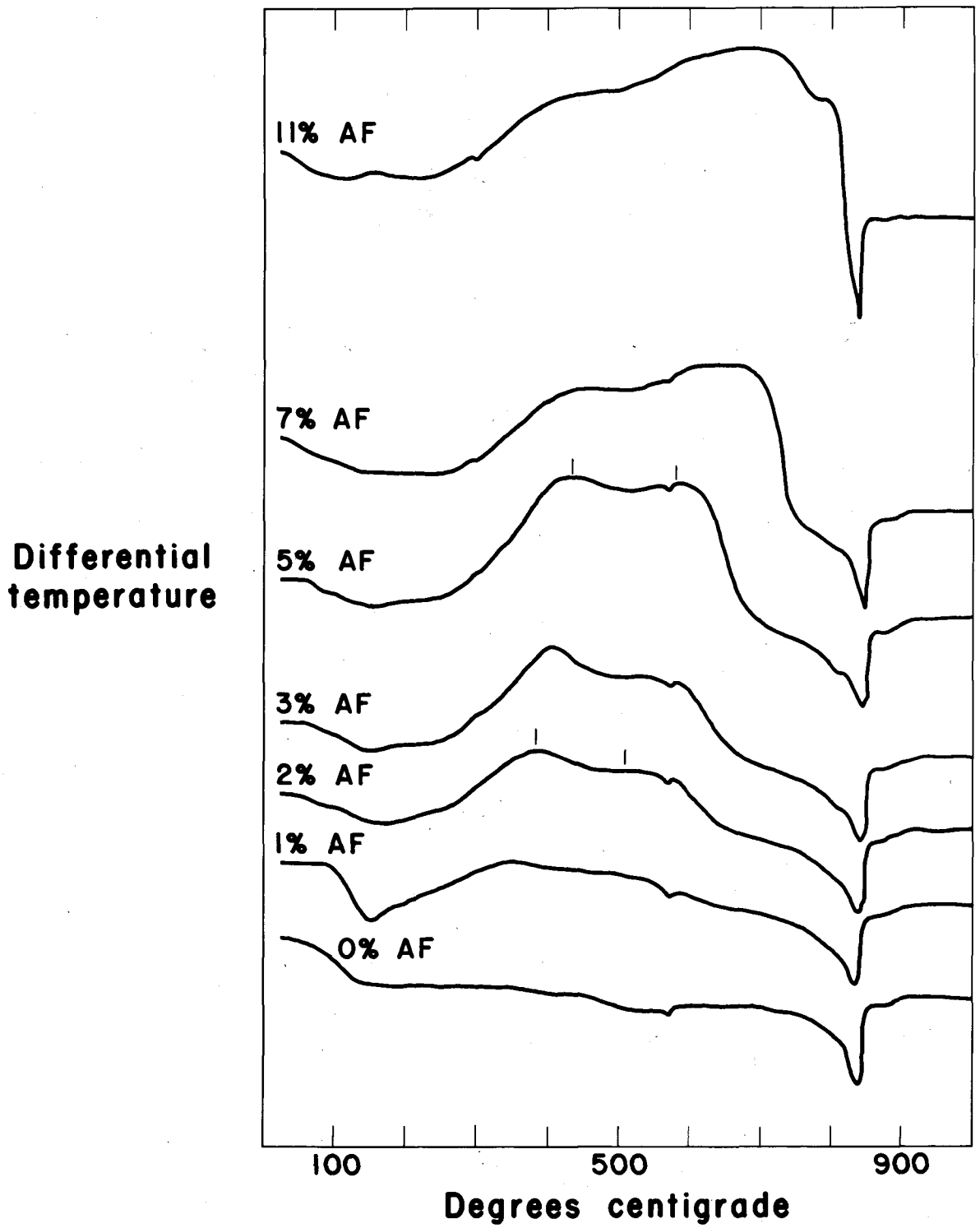

11% AF
7% AF
5% AF
3% AF
2% AF
1% AF
0% AF
Differential temperature
100
500
900
Degrees centigrade

Figure 23. Differential thermal curves for loess sample 36-1 stabilized with various percentages of aniline-furfural as indicated on the left hand side of the curves

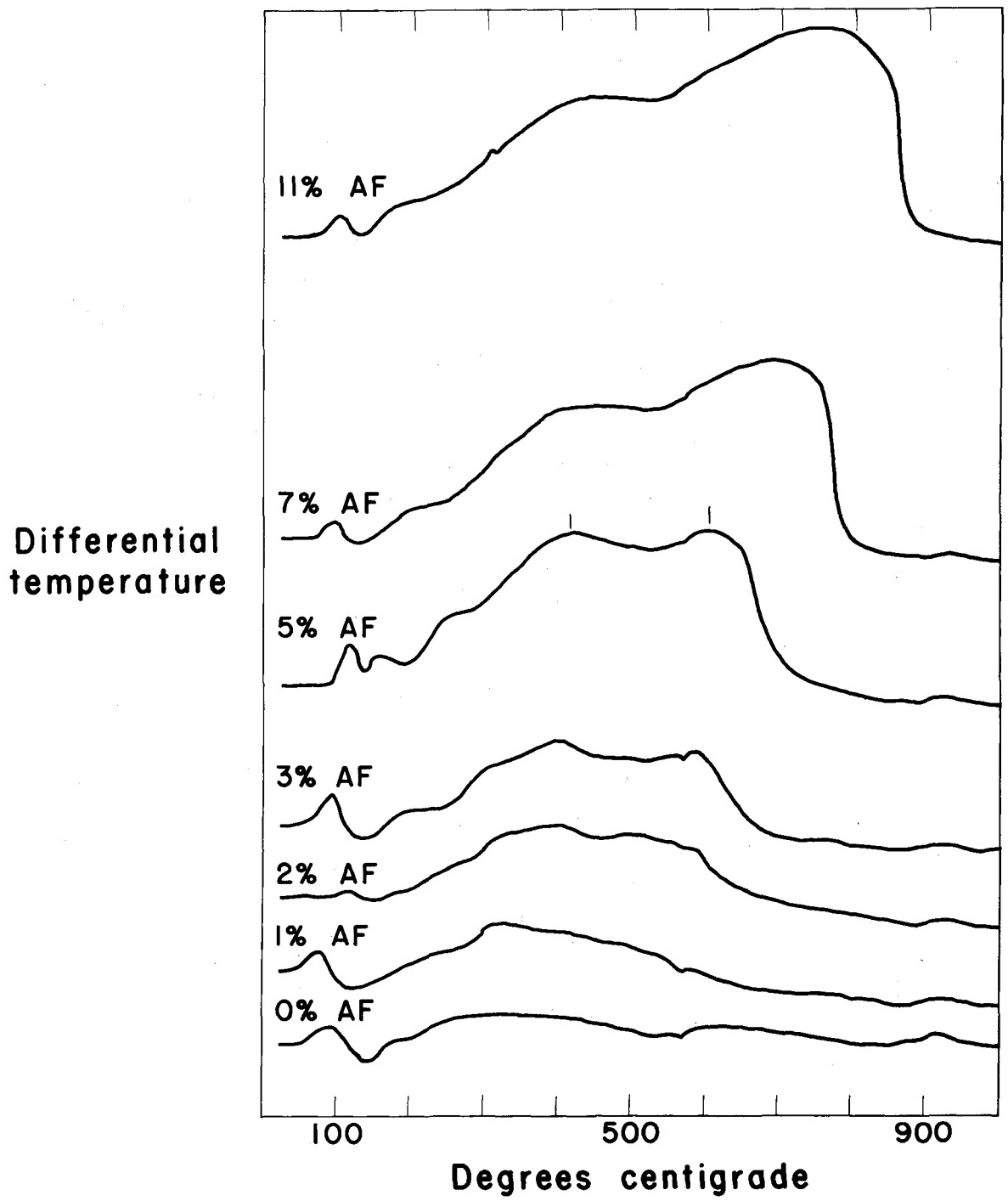
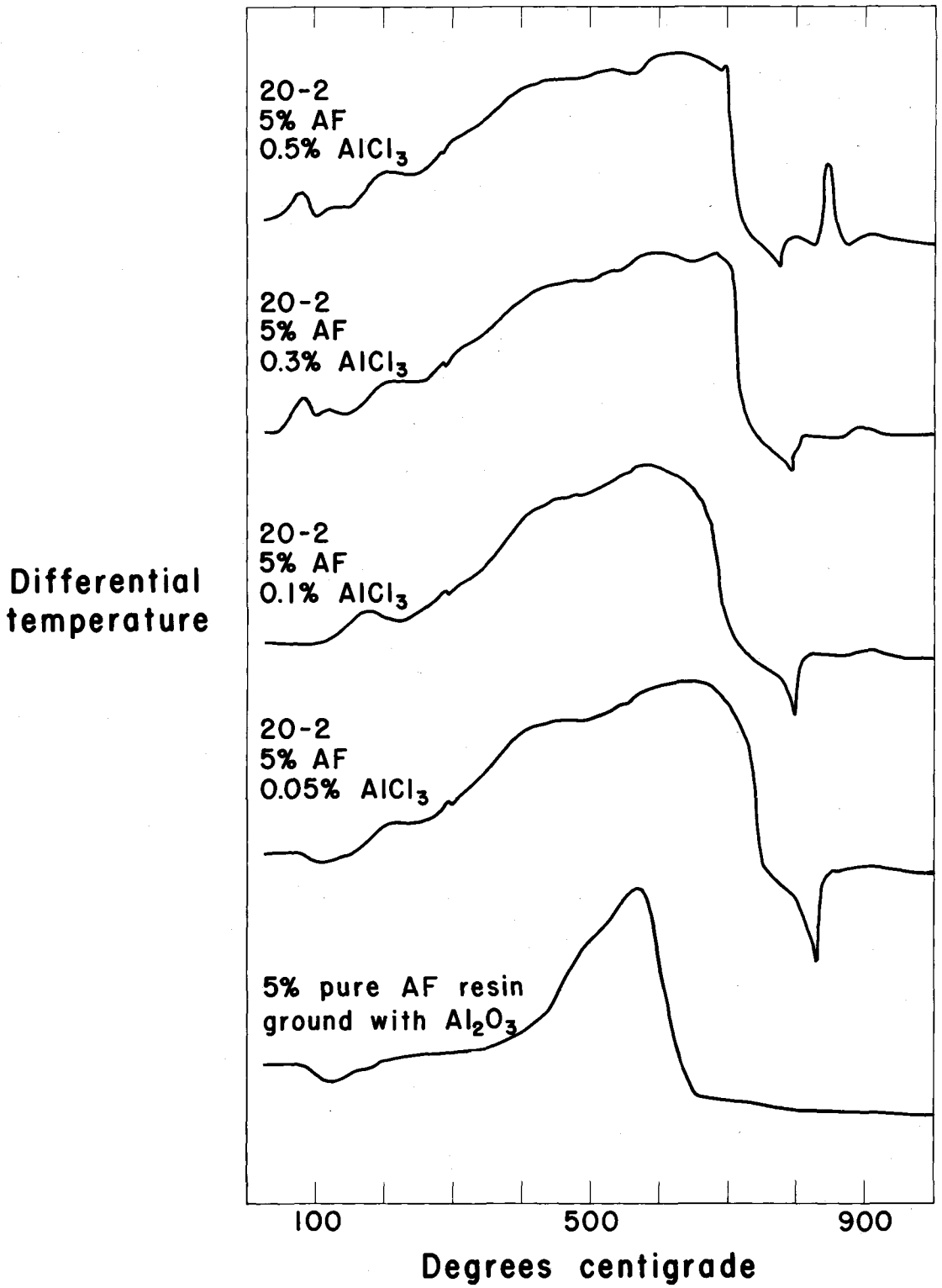

11% AF
7% AF
5% AF
3% AF
2% AF
1% AF
0% AF
Differential temperature
100
500
900
Degrees centigrade

Figure 24. Differential thermal curves for loess sample 20-2II stabilized with 5 per cent aniline-furfural using varying amounts of aluminum chloride catalyst. The amounts of catalyst used are shown on the left hand side of the curves. The lower curve is from a synthetic sample in which pure aniline-furfural resin was ground with alumina so as to form a mixture containing 5 per cent of the resin


20-2
5% AF
0.5% AlCl3
20-2
5% AF
0.3% AlCl3
20-2
5% AF
0.1% AlCl3
20-2
5% AF
0.05% AlCl3
5% pure AF resin
ground with Al2O3
Differential
temperature
100
500
900
Degrees centigrade

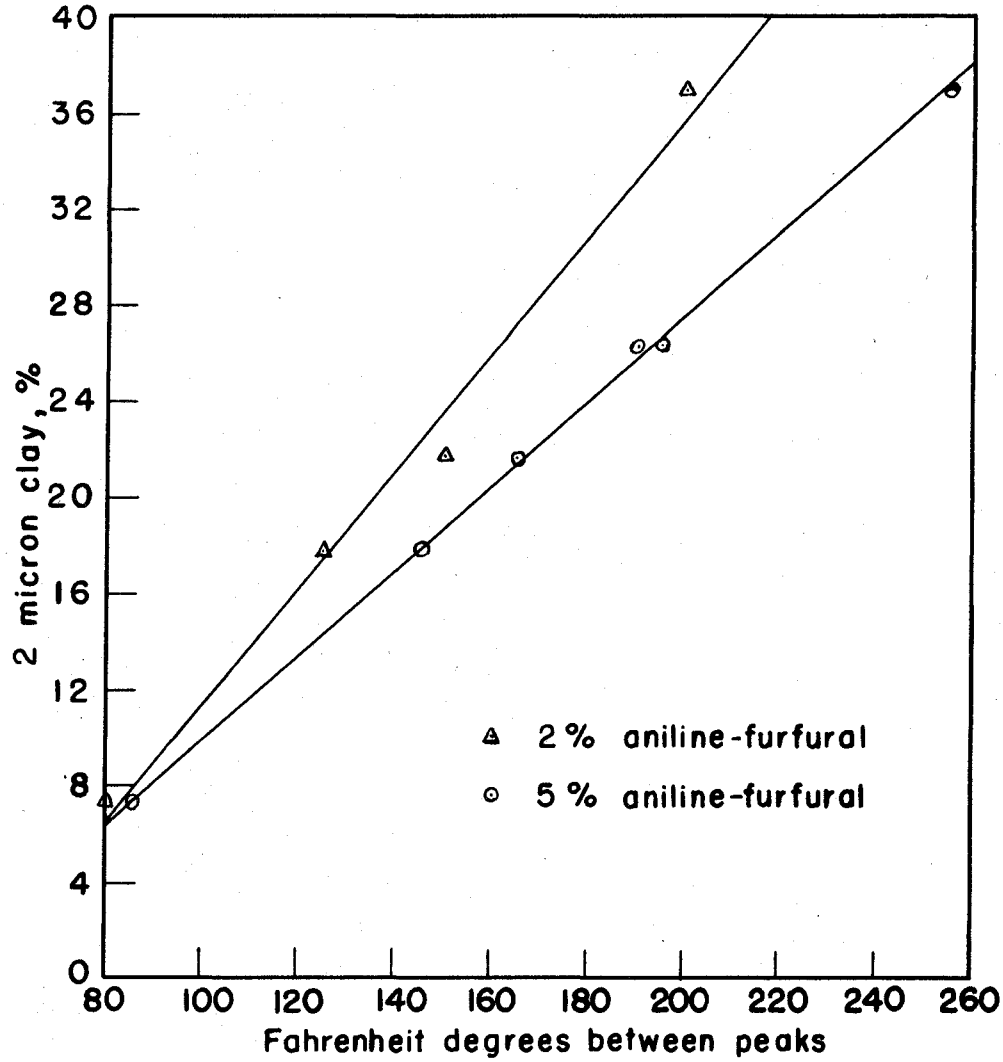


Figure 25. 2 micron clay content of loess stabilized with 2 and 5 per cent aniline-furfural plotted against the Fahrenheit degrees between the double exothermic peaks found on the differential thermal curves

of reacting material present is given by Kerr et al (21) in a preliminary report for the American Petroleum Institute on reference clay minerals. The areas under the left and right peaks were determined with a planimeter and plotted against the resin content for soils 20-2II and 36-1. These plots are shown in Figures 26a and 26b. The area under the left peak tends to reach a maximum in both cases at about 5 per cent resin content. The constant area indicates a constant amount of resin involved and is believed to be caused by a maximum amount of aggregation, due to clay-resin complexes, being reached. This means that a maximum amount of specific surface, based on aggregate volume, is presented.

The area under the right hand peaks is also plotted against the resin contents in Figures 26a and 26b. The plots show a linear relationship between these two variables. The second peak is thought to be caused by adsorbed resin and the resin that binds the aggregates of soil particles together. The higher the resin content the larger the amount of resin retained within the aggregates. In grinding the specimens for analysis the weakest and thinnest resin bonds are broken and exposed. These surfaces are then the first to be burned. The resin held within an aggregate particle and within the clay minerals becomes exposed only after the breakdown of the clay mineral structure occurs at about 550 degrees. Shrinkage usually accompanies this breakdown and

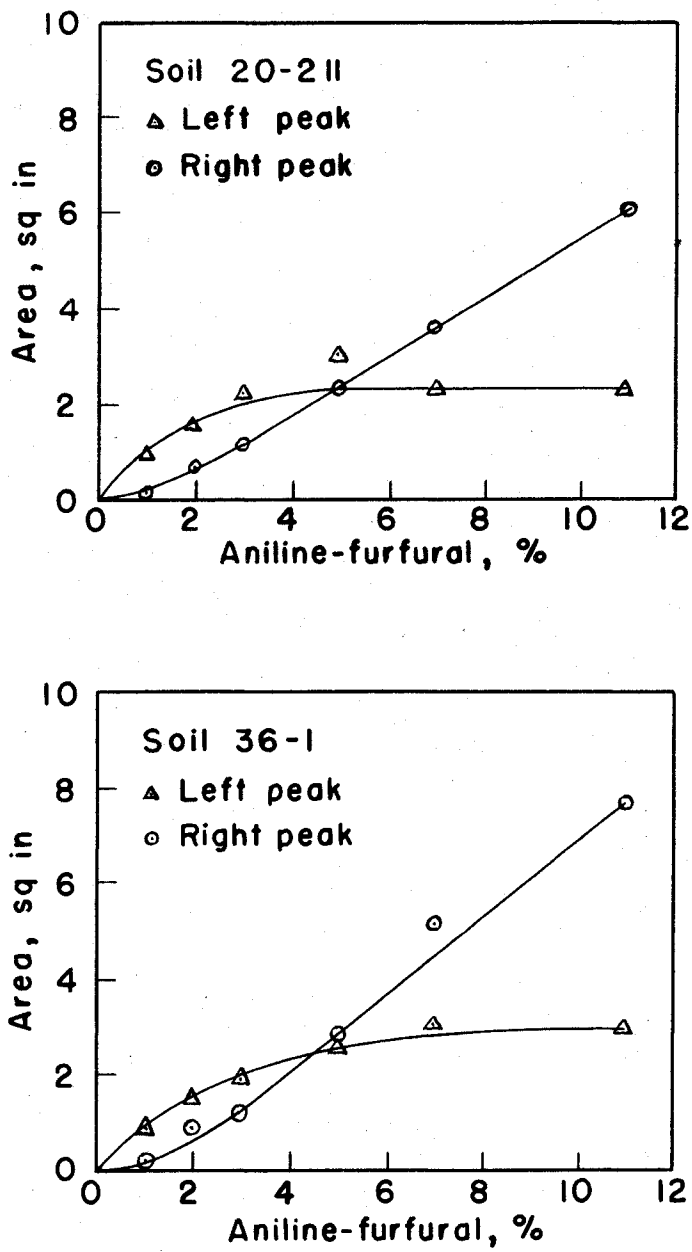


Figure 26. The areas under the left and right peaks on differential thermal curves plotted against the aniline-furfural content. Figure 26a (top graph) is for soil 20-2II; Figure 26b (lower graph) is for soil 36-1

would thus break the minerals away from the resin and possibly disintegrate the aggregate particles.

The thermal curves in Figure 24 were obtained from specimens that had been treated with aluminum chloride catalyzed aniline-furfural. A small enothermic reaction appears in these curves at about 300 degrees Centigrade. A reaction of this type usually indicates a structural change. Since the aluminum chloride catalysis seems to produce a slightly stronger and more brittle product it is believed that the resin is more highly cross-linked than the non-catalyzed resins. The presence of this endothermic reaction in several of the higher resin contents seems to indicate that the quantity of resin used is enough to create enough heat to produce some cross linking.

The lower curve in Figure 24 is shown to illustrate that a double peak does not occur when the resin is associated with a material devoid of clay minerals. The only reaction taking place, as shown by the curve, is the burning of the organic resin. Initial combustion is slower and does not reach a peak quite as rapidly as it does in stabilized soil since the resin in the synthetic sample is ground while that in the soil has been formed in situ. The particles of ground resin are much thicker than the resin held by the clay or between soil particles.

Atterberg Limits

The Atterberg limits were determined for six soil samples that had been stabilized with different percentages of aniline-furfural. Considerable difficulty was experienced in getting the water to mix with the stabilized material. As much as 30 minutes of kneading and mixing with a spatula was required. Data are tabulated in Table 13.

The results show that a small amount of resin greatly reduces the plasticity index in all cases. Additional resin reduces the plasticity index still more until finally the material becomes non-plastic. The use of the Atterberg limits is one basis by which treated specimens can be compared to non-treated specimens as to water holding capacity. They also present a good method for waterproofing evaluation.

Freezing and Thawing

All samples were subjected to freezing and thawing cycles with three samples being tested at the end of 1, 2, 3, 4, 6, and 9 cycles. The remaining three samples were set aside after the ninth cycle and allowed to air-dry for 30 days before being subjected to a tenth and final cycle. Data obtained are tabulated in Table 14. The strength tabulated after zero cycles is the air-dry strength of the soil and

Table 13. Atterberg limits of stabilized and non-stabilized soils

Sample no.	Aniline-furfural content %	Liquid limit %	Plastic limit %	Plasticity index %
55-1	0	29.6	27.3	2.3
	2	NP*	-	NP
	5	NP	-	NP
20-2II	0	33.2	24.0	9.2
	1	27.6	24.0	3.6
	2	25.0	22.4	2.6
	3	26.3	24.3	2.0
	5	NP	-	NP
	7	NP	-	NP
	11	NP	-	NP
26-1	0	34.7	24.0	10.5
	2	26.6	25.1	1.5
	5	24.8	21.0	3.8
36-1	0	39.0	25.6	13.4
	1	32.0	23.0	9.0
	2	30.9	24.2	6.7
	3	29.7	24.8	4.9
	5	NP	-	NP
	7	NP	-	NP
	11	NP	-	NP
46-1	0	54.7	22.0	32.7
	2	33.8	26.4	7.4
	5	29.8	25.1	4.7
503-2	0	56.7	26.4	30.3
	2	37.7	29.5	8.2
	5	31.9	27.9	4.0

*Non-plastic

Table 14. Data obtained from freezing and thawing tests

Soil and amount of resin treatment		Cycle no.	Moisture absorbed %	Height increase inches x 1000	Strength lbs
20-2II	5%	0			2600
		1	1.4	4	1320
		2	1.7	1	1450
		3	1.8	4	1210
		4	1.7	4	1030
		6	2.5	5	1080
		9	2.6	4	970
		10*	0.8	0	1360
20-2II	2%	0			2090
		1	2.0	1	490
		2	2.3	0	500
		3	2.8	4	390
		4	2.9	6	390
		6	3.1	5	420
		9	3.7	8	290
		10*	1.4	2	460
36-1	5%	0			3380
		1	1.8	4	1930
		2	2.3	3	1730
		3	2.6	9	1460
		4	2.9	10	1370
		6	3.9	13	1080
		9	4.3	16	970
		10*	1.6	7	1770

*30 days of air-drying between cycles 9 and 10

treatment indicated.

The moisture absorbed was calculated as the gain in weight above the air-dry weight of the sample and is based on the stable weight. Very little moisture is absorbed as shown. This is thought to account for the remarkable

durability of the samples. There was no spalling or sample disintegration noticed. However, the samples became slightly soft where they were in contact with the moist felt pads and suffered some mechanical abrasion due to handling.

The strength of the samples rapidly decreases with the first cycle but appears to trend toward a constant value thereafter. The period of drying after the ninth cycle caused the strength and moisture absorption to revert to nearly the same values found after the first cycle.

The condition of the samples after nine cycles may be seen in Figure 27. The samples number 14a-15 and 14b-7 exhibit the typical abrasion loss at their bases.

Wetting and Drying

The specimens used in this study were subjected to the identical number of wet and dry cycles as were employed in the freeze-thaw study. Table 15 shows the results obtained from this study with the air-dry strength shown for comparisons.

The strength, like that of the wet-dry specimens, tends to drop considerably with the first cycle and remain relatively constant thereafter. The samples, however, did not show any significant changes after the 30 day drying period.

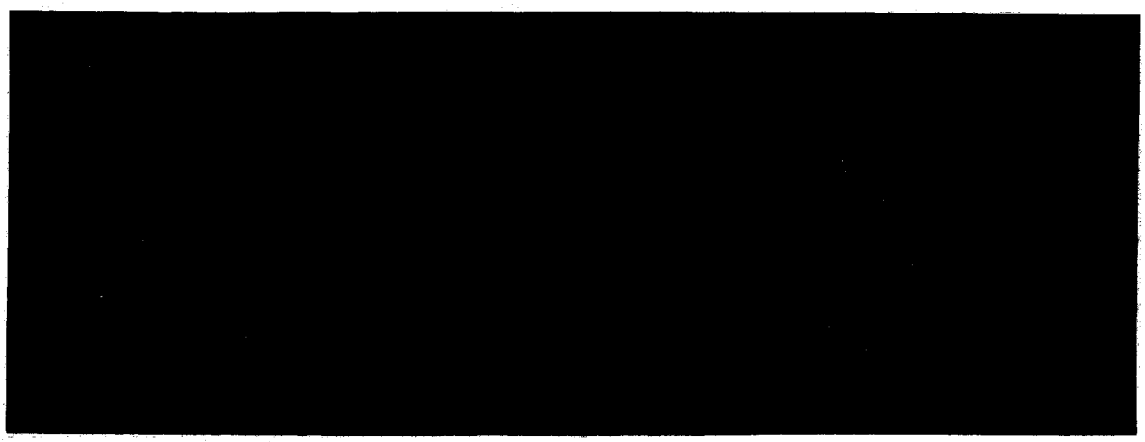


Figure 27. Photograph of wet-dry specimens on the left and freeze-thaw specimens on the right, after nine cycles in each case. Reading from left to right the first three rows are: soil 20-2II with 5 per cent resin, soil 20-2II with 2 per cent resin, soil 36-1 with 5 per cent resin. The second three rows are arranged in the same order

Table 15. Data obtained from wetting and drying tests

Soil and amount of resin	treatment	Cycle no.	Moisture absorbed %	Height increase inches x 1000	Strength lbs
20-2II	5%	0			2600
		1	3.7	6	860
		2	4.2	9	730
		3	5.1	9	750
		4	3.7	12	780
		6	4.1	11	760
		9	3.8	12	770
		10*	4.0	11	740
20-2II	2%	0			2090
		1	3.9	8	395
		2	4.0	9	330
		3	4.9	12	310
		4	4.5	11	290
		6	5.0	9	280
		9	4.6	11	320
		10*	4.9	9	260
36-1	5%	0			3380
		1	2.8	13	1250
		2	5.7	25	870
		3	7.6	23	650
		4	6.7	25	700
		6	7.8	28	570
		9	8.1	28	500
		10*	7.4	24	590

*30 days of air-drying between cycles 9 and 10

Apparently some of the resin or the unreacted material is leached from the specimens during the immersion periods. A distinct amber color was noticed in the immersion water. The depth of coloring became more pronounced with each cycle. This discoloration is most probably due to unreacted material since resins are usually not water soluble. The immersion

water also had an odor typical of aniline-furfural.

Figure 27 is a photograph of some specimens after nine cycles. Samples 14e-8 and 14e-15 show some shrinkage cracks that are typical of those that appear in higher clay content soils. These cracks did not appear to be serious and no bad effects could be allayed to them.

The number of cycles of freezing and thawing and wetting and drying employed in these studies are considered to be very severe weathering tests for 2 x 2 specimens. Winterkorn (44) has reported that four cycles with 2 x 2 specimens is about equivalent to 12 cycles with the 4 x 4⅝ standard Proctor specimens used in the freeze-thaw and wet-dry testing of soil cement. The durability of the aniline-furfural treated soil specimens when subjected to nine cycles in both tests is therefore quite remarkable.

Microscopic Examination

Examination of stabilized samples under a low power binocular microscope revealed some interesting things. The soil particles appear to be well aggregated with the degree of aggregation varying from soil to soil. It also appears that the aggregates are surrounded and interlaced with resin.

The homogeneity of the overall soil-resin mass is very good for the soils that are low in clay content. Higher clay content soils contain some aggregates that are surrounded by

resin but are devoid of resin in their centers. Fracture planes that were examined revealed that the resin bonds between aggregates and the aggregates themselves failed in shear. These planes present a picture not at all unlike a cobble-stone street when viewed under a microscope.

Economic Discussion

Availability and cost are two of the most important factors in any contemplated use of chemical materials. Since the use of aniline-furfural as a soil stabilizer would involve considerable quantities of both chemicals the question of availability arises. A preliminary report of the Tarriff Commission shows a production of 132 million pounds of aniline in 1955 (30). Present day production of furfural is about 50 million pounds per year.

Aniline and furfural in carlots cost $0.22 and $0.13 per pound respectively in March of 1956 (30). This places the cost of a 2:1 resin at $0.19 cents per pound. A table of cost comparisons for various stabilizing agents has been prepared from data supplied by personnel of the Iowa Engineering Experiment Station who have been working with the chemicals listed.

The comparative costs are listed together with strength after 24 hours immersion, the amount of treatment, and the

Table 16. Economic comparisons of various stabilizing treatments for soil 20-2

Stabilizing material	Treatment %	Cost cents per lb	Strength after 24 hours immersion lbs	Stabilization cost cents per 100 lbs of soil
Aniline-furfural	1	19	530	19
	2	19	810	38
	3	19	980	57
Cutback asphalt	10	2.41	220	24
Portland cement	15	1.111	1780	16.7
Lime-Fly ash (1:2)	18	0.58	485	10.5
Hydrated lime	6	1.125	250	6.7
Arquad 2 S	0.16	43	310	6.7
Crude amine	0.30	18	260	5.3
Armeen residue	0.38	9	330	3.5
Arquad 2 HT	0.08	36	330	2.7

cost of stabilizing 100 pounds of soil in Table 16. Stabilization of soil with aniline-furfural is one of the most expensive treatments listed. However, the benefits derived from the use of aniline-furfural could well justify the extra cost. It is conceivable that aniline-furfural stabilization could be used in conjunction with a cheaper method of stabilization in building roads. The more economical method making up the majority of the stabilized material and

aniline-furfural being used in areas of critical moisture situations.

Lower grades of either aniline or furfural are not available because of the very nature of the processes by which they are made. The manufacturers find that they are able to sell the purer products cheaper than they can sell the chemicals containing water. This is due to the cost of transporting the inert water with the chemicals.

Furfural plants which are located in Omaha, Nebraska and in Cedar Rapids, Iowa should facilitate the use of aniline-furfural resin in Iowa. Furthermore, any widespread usage of the resin as a road building material could enhance the economic aspects of the Iowa farmer since furfural is made from agricultural products.

THEORETICAL INTERPRETATIONS

It appears that a theoretical mechanism of aniline-furfural stabilization of Iowa loess may be established from the data. The stability seems to be primarily due to the phenomena of absorption and adsorption of the chemicals by the montmorillonite type clay minerals predominant in the clay fraction. The theory being that some resin is formed, within the expanding lattice of the clay minerals, from absorbed chemicals and that some resin is also formed by a reaction between adsorbed and free chemicals. The latter reaction would tend to produce a resin mass that encloses and cements the soil grains and the soil aggregates.

Evidence that the theory is correct is pointed out in the following discussion of the chemicals involved, the soil, the laboratory data, and phenomena observed by other authors.

The reaction between aniline and furfural produces large organic cations as discussed by Gieseking (18, p. 75). He further states that a 2 per cent treatment of soils should be sufficient to saturate all soils except those of the very highest cation exchange capacities. Large organic cations of aniline-furfural held in the exchange positions should be able to enter into polymerization reactions by virtue of their unsaturated double bonds and therefore be linked to

other aniline-furfural cations held in other exchange positions. This would create a bond between clay minerals and aggregates of soil particles.

Jordan (19) has observed that furfural is more highly absorbed by clay minerals than aniline. Furfural is also more soluble in water than aniline. Bearing these two facts in mind it will be recalled that the mixing study has revealed that the introduction of water and furfural before aniline produces the most satisfactory results. Evidently more resin is formed between the unit layers of the clay minerals when this mixing procedure is used. Since furfural is more soluble in water than aniline, the introduction of furfural first should tend to provide the most uniform distribution and absorption of chemicals.

The low curing shrinkage and the low amount of swelling on curing may be explained by this theory. The formation of a resin between the unit layers of the clay minerals would tend to hold the layers apart in an expanded position even after moisture removal, accounting for the low amount of shrinkage exhibited. Conversely the reentry of moisture would provide little or no expansion since the clay minerals would already be in an expanded state.

The low moisture absorption and hydrophobic character of the aniline-furfural stabilized soils are also consistent with the theory. Saturation of the cation exchange sites with

large organic cations to produce hydrophobic qualities has been discussed by Davidson (4) and Gieseking (18, p. 75). The aniline-furfural reaction products include such cations and the hydrophobic character of loess stabilized with aniline-furfural is well illustrated by the weathering tests previously discussed. Moisture does find its way into the clay minerals but in small quantities only. The volume of available space is no doubt a large contributing factor to the magnitude of water absorption. Any resin formed between the unit layers of the clay minerals and in the void spaces of the soil mass would prevent moisture from occupying these positions. Therefore the amount of moisture absorption would be reduced below that encountered before stabilization.

The formation of resins between the unit layers of the clay and on the clay is supported by the results of the differential thermal analysis. The area under the right hand peak of the thermal curves becomes larger with an added amount of resin, indicating that more resin is formed in close association with the clay. The shift of the right hand peak toward the right with increased clay content also indicates that more resin is released for combustion after the clay decomposition. Therefore the resin must have been held by a bond between the clay and the resin.

The steady gain of wet strength and of dry strength, after the initial loss due to cohesion destruction, supports

the reasoning that an enclosure and cementing of soil grains and aggregates occurs. Increased resin content would tend to increase the thickness of the enclosing and cementing wall, thus increasing the overall strength of the stabilized soil.

According to this theory stability should increase with an increase in clay content. However, the data indicate that the optimum stability occurs in the mid range of clay content. There is an indication that aggregation of treated soil also increases with clay content. In soils having clay contents above that which produces maximum stability the aggregation appears to be increased so that total or near total saturation of the clay minerals with the resin is prevented. This tends to reduce the effectiveness of the overall stabilization of a soil with a high clay content by leaving some soil in the aggregates untreated as was found to be true by visual inspection of fracture planes.

SUMMARY AND CONCLUSIONS

Natural gravel sources in some areas of the United States are being rapidly depleted due to extensive secondary road construction and maintenance. Southwestern Iowa is such an area. The loess deposits of southwestern Iowa are very extensive and offer a possibility as a road building material if the soil can be suitably stabilized for all weather roads.

The Iowa Engineering Experiment Station is conducting extensive research to uncover possible loess stabilization methods. The primary objectives of this investigation have been to evaluate aniline-furfural as a stabilizing agent for the loess of southwestern Iowa.

The following conclusions are made on the basis of observations and results of the investigation. It is believed that the conclusions should in general apply to all soils of similar textural and mineralogical composition.

1. The moisture-density relationship of aniline-furfural stabilized soils should be investigated for every proposed soil.

2. Aniline and furfural can not be regarded as liquids that replace equal volumes of water in the density requirements.

3. A mol ratio of 2 mols aniline to 1 mol furfural produces the best results. Weight ratios between 3:2 and 5:2 may be used without excessive loss of effectiveness.

4. Water and furfural should be mixed with the soil first to produce optimum results. The order of the water and furfural is not of considerable importance but in any case aniline should be mixed in last.

5. Drying is nearly complete after five days of air curing and has reached equilibrium after eight days of air curing.

6. The strength has reached a near final value after four days of air curing. The strength increases further but then recedes to approximately the four day value after 10 days air curing.

7. Aluminum chloride catalyzes the reaction and decreases the density obtainable with any given treatment of aniline-furfural.

8. Strengths obtainable with aniline-furfural are sensitive to moisture content at compaction. Optimum moisture content for maximum density and optimum moisture for maximum strength do not always coincide.

9. Small quantities of aniline-furfural reduce the dry strength of the soil treated.

10. The wet strength of treated soils increases with increased amounts of treatment.

11. The wet strength exhibits a maximum value for a constant amount of aniline-furfural treatment in loess soils having a 2 micron clay content of about 22 per cent.

12. Moisture absorption is the lowest for loess soils having a 2 micron clay content between 18 and 26 per cent and treated with from 2 to 5 per cent aniline-furfural.

13. Aniline-furfural is very closely associated with the clay in a soil and is probably polymerized on and in the clay minerals.

14. Small amounts of aniline-furfural treatment greatly reduce the plasticity of a soil.

15. Aniline-furfural treated specimens are very resistant to freezing and thawing although a strength loss is suffered. This loss is apparently regained after moisture removal by drying in above freezing temperatures.

16. Alternate wetting and drying produces a permanent strength loss in aniline-furfural treated specimens.

17. Aniline-furfural treatments must be 2 per cent or less in order to be economically competitive with other methods of stabilization.

18. A more efficient method of mixing should be developed in order to obtain maximum returns for a given resin treatment in soils with high clay contents.

19. All failures resulting from unconfined compression testing were due to shear failure.

20. Aniline-furfural treatment shows evidence of being beneficial to the all-weather stability of Iowa loess. The amount of treatment required may not be economically competitive with other methods of soil stabilization.

21. The success of aniline-furfural treatment is dependent on the clay content of the soil. High and low clay contents giving the least satisfactory results.

22. Aniline-furfural treatment of soils reduces their permeability by filling voids with resin and by making the clay hydrophobic.

The beneficial effects of aniline-furfural treatment are easily apparent since all untreated specimens failed on immersion in water. Even the lowest resin treatment imparts a significant wet strength to all textures of soil studied. This ability to increase the hydrophobic qualities of the soil while developing a wet strength of significant magnitude seems to be the most outstanding stabilizing property of the resin.

Aniline-furfural stabilized loess was very resistant to all laboratory weathering tests employed and is one of the best soil stabilizing agents investigated to date in this laboratory. The treatment shows strong evidence of being beneficial to the all-weather stability of Iowa loess.

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